

Generation of water-soluble organic acids from kerogen during hydrous pyrolysis: implications for porosity development

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Abstract

Concentrations of organic acids ranging up to several thousand parts per million have previously been found in oil-field waters. These acids are of interest because of their potential to enhance porosity by the dissolution of carbonates and aluminosilicates. They are believed to be generated from organic geopolymers (kerogen) in the late-diagenetic-early-catagenetic stage of thermal maturation.

During the course of artificial maturation experiments in which kerogens of varying type were heated in the presence of water (so-called 'hydrous pyrolysis') and different minerals, the distribution and abundance of low molecular weight water-soluble acids were determined by gas chromatography and gas chromatography-mass spectrometry. Preliminary results suggest that significant quantities of mono- and di-carboxylic acids are produced during hydrous pyrolysis. The amounts and types of acid appear to vary as a function of kerogen type, maturity and mineralogy. Implications of these findings regarding the development of secondary porosity are discussed.

KEYWORDS: organic acids, kerogen, hydrous pyrolysis, porosity development.

Introduction

THE capacity of sandstones to act as reservoirs for crude oil has an important bearing on the success of oil exploration. This capacity is chiefly a function of rock porosity. Many reservoir rocks from which crude oil is currently produced exhibit enhanced chemically-generated 'secondary' porosity which is thought to result from mineral leaching by aggressive pore water solutions (Hayes, 1979; Schmidt and McDonald, 1979, and refs therein; McBride, 1980). The discovery of high concentrations of organic acids in numerous oil-field waters has led to the suggestion that these may

be the components responsible for many of the textural characteristics of reservoir sandstones (Carothers and Kharaka, 1978; Schmidt and McDonald, 1979). In the shallow sub-surface such acids could be introduced to reservoir rocks through the ingress of meteoric waters or through the migration of solutions containing the acidic products of petroleum biodegradation, whereas it has been postulated that oxidation of kerogen may be more important at greater depths (Bonham, 1980; Schmidt and McDonald, 1979). However, experimental evidence for the latter process is scant and limited to the results of a few very recent studies (Surdam *et al.*, 1984; Kawamura *et al.*, 1986; Cooles *et al.*, 1987).

TABLE 1. Geochemical description of kerogens together with the yields of C₂-C₁₀ acids (a) extractable by treatment with 0.005M KOH and (b) released during hydrous pyrolysis (330°C, 72 hr).

KEROGEN	GEOCHEMICAL CHARACTERISTICS				C ₂ -C ₁₀ ACIDS (mg/g KEROGEN)					
	ATOMIC RATIOS		KEROGEN TYPE	MATURITY (%Ro)	0.005M KOH EXTRACTABLE			RELEASED DURING HYDROUS PYROLYSIS*		
	H/C	O/C			A) MONO-CARBOXYLIC	DI-CARBOXYLIC	TOTAL	B) MONO-CARBOXYLIC	DI-CARBOXYLIC	TOTAL
KIMMERIDGE CLAY (Blackstone Band)	1.20	0.09	II	0.35	0.13	-	0.13	4.13	0.28	4.41
GREEN RIVER SHALE (Mahogany Zone)	1.56	0.10	I	Low	0.19	-	0.19	0.36	0.30	0.66
NEW ALBANY SHALE	1.06	0.14	II/III	0.47	0.23	-	0.23	0.74	0.12	0.86
GUTTENBURG OIL ROCK	1.48	0.10	I	0.42	0.20	-	0.20	1.47	0.03	1.50
MONTEREY SHALE	1.46	0.25	II	0.26	0.12	-	0.12	5.60	0.17	5.77

*330°C, 72 HRS

In the present study we have conducted a series of aqueous heating experiments on five kerogens in the presence of various minerals to provide further evidence for the generation of acids by kerogen oxidation. The aims of the experiments were: (1) to observe whether organic acids were produced in significant amounts by the heating of kerogens; (2) to investigate the effects of different experimental heating times and temperatures; and (3) to investigate the effects of minerals on the amounts and type of acids produced.

This paper presents preliminary results from a study of the aqueous products from these 'hydrous pyrolysis' experiments. It forms part of a larger investigation into the behaviour of kerogens during artificial maturation and a more detailed description of the acidic and other maturation products will be provided elsewhere (Eglinton *et al.*, 1986a, b and c).

Experimental

General. All solvents used, including water, were distilled in glass. KOH was fused (500°C, 2 hr) prior to use. Reagents were solvent-extracted where possible, and all glassware was cleaned in chromic acid and rinsed in distilled water before use. Procedural blanks were performed routinely.

Organic-rich shale samples (Kimmeridge, New Albany, Green River, Guttenberg, Monterey) were cleaned, powdered (Tema disc mill) and extracted (Soxhlet; dichloromethane:methanol,

93:7, 72 hr) to remove organic-soluble material. Kerogens were then freed from their mineral matrices by a hot hydrochloric and hydrofluoric acid treatment followed by re-extraction (Soxhlet, DCM:MeOH, 93:7, 72 hr).

The isolated kerogens were subjected to elemental and optical analyses. Details of kerogen properties are given in Table 1. All minerals used were powdered, solvent extracted and examined by XRD to detect any impurities (Eglinton *et al.*, 1986c). Similar analyses were also performed on the heated residues.

Heating experiments. Heating experiments were carried out in purpose-built 35 ml 316 grade stainless steel 'bombs'. Typically, kerogen (250 mg) or a kerogen-mineral mixture (1:20 w/w) was placed in the 'bomb', distilled H₂O (11 ml) was added and air was removed by purging with nitrogen prior to closure. Vessels were sealed with a copper gasket. The 'bombs' were placed in a commercially available pressure reactor (1 litre, Parr Instrument Co.) also part-filled with water (in order to minimize the pressure differential across the bomb walls and to reduce temperature gradients in the system) which was sealed in turn. The 11 vessel was equipped with a pressure gauge and rupture disc for safety purposes. The temperature of the reactor was raised by a heating coil and regulated by a thermocouple linked to a controller ($\pm 5^\circ\text{C}$). The low-temperature pyrolysis experiments (200 and 250°C) were performed in the bombs in a gas chromatograph oven rather than in the Parr reactor. Samples were heated rapidly to the

desired temperature (200–340 °C) and held isothermal for the required period (7.2–720 hr) after which the 'bombs' were allowed to cool prior to opening.

Extraction and analysis. The contents of each 'bomb' were transferred to a separatory funnel and partitioned into organic-soluble and aqueous-soluble products using distilled H₂O (25 ml), dichloromethane (4 × 20 ml), methanol (5 ml) and light petroleum (4 × 50 ml). The combined organic-soluble extract was removed for separate analysis (Eglinton *et al.*, 1986c), and the aqueous phase was centrifuged (3000 rpm, 15 min). The supernatant liquid was filtered (Whatman No. 5, 7.0 cm), poisoned with HgCl₂ (c. 1–2 mg) and stored under nitrogen at 4 °C prior to analysis. Residual solid organic material was also analysed separately (Eglinton *et al.*, 1986b).

Water-soluble acids were analysed by a modification of the methods described by Lambert and Moss (1972) and Kawamura *et al.* (1985). Briefly, the pH of the aqueous extract was adjusted (c. 8–9, 1M KOH) before drying using a combination of rotary evaporation under reduced pressure (50 °C) and evaporation using a stream of dry nitrogen. BF₃/*n*-Butanol (0.33 ml, 14% v/v, Chrompack) was added, and after ultrasonication (2 min), the mixture was heated in a water bath (100 °C, 30 min) to complete esterification. Unreacted *n*-butanol and acids containing hydroxyl groups were converted to trifluoroacetates by the addition of trifluoroacetic anhydride (0.33 ml, 10 min, room temperature). The resultant esters were dissolved in dichloromethane (5 ml) and washed with distilled H₂O (2 × 5 ml), before analysis by gas chromatography (gc) and gas chromatography–mass spectrometry (gc–ms).

GC of the esters was performed on a Carlo Erba 4160 instrument using on-column injection and a 5% phenylmethylsilicone fused silica column (25 m × 0.33 mm i.d., Hewlett Packard) with hydrogen as carrier gas and a temperature programme of 40–300 °C at 4 °C min⁻¹ (final temperature, 10 min). Peak areas were measured with a Hewlett-Packard 3390A Integrator. Concentrations of individual acids were determined directly from chromatograms. Procedural blanks contained no measurable dicarboxylic acids (<1 µg g⁻¹) and levels of monocarboxylic acid contaminants were, in all cases, less than 10% of the actual samples.

GC–ms was carried out on a Carlo-Erba 5160 gas chromatograph interfaced to a Kratos MS-25 mass spectrometer (electron energy 40 eV). Injections were made on-column onto a fused silica column (30 × 0.21 mm i.d.) coated with DB-1 (J & W) with a temperature programme of 40 °C

(5 min; 40–300 °C at 4 °C min⁻¹ and helium as carrier gas).

Results and discussion

The kerogens used for the maturation experiments were all initially relatively immature, as indicated by vitrinite reflectance values of 0.35–0.47 and represented a range of types (Table 1). These were carefully chosen in order to avoid the use of organic matter that had already suffered significant geological maturation and also so that the influence of kerogen type on acid generation could be observed.

All of the heating experiments produced organic acids. The distribution of acids, was revealed by gc (and gc–ms of some samples) and a typical gas chromatogram is shown in Fig. 1. Whilst the major component by far in virtually all of the experiments was acetic acid (see Table 3), many other longer chain mono-, dicarboxylic and aromatic acids were present (Fig. 1). The components identified are listed in Table 2.

In all samples, there was a sharp drop-off in the concentrations of both mono- and di-carboxylic acids with increased carbon number. This probably reflects decreasing solubility with increasing carbon chain length.

Fig. 2 shows the variation in total (C₂–C₁₀) acid concentration with pyrolysis temperature for Kimmeridge kerogen heated for 72 hours. Moderate acid generation was observed at pyrolysis temperatures below 280 °C. Above this temperature total acid yields are seen to rise sharply to amounts in the order of 4 mg g⁻¹ after which no further increase is apparent. Maximum generation occurred at 330 °C and this temperature was also used to study the acid-producing potential of other kerogens.

The amounts of acids produced by heating different kerogens at 330 °C for 72 hr varied from 0.66 to 5.77 mg g⁻¹ kerogen (Table 1). Thus it is evident that oxidation of kerogen does occur during artificial maturation. Furthermore, kerogen type does appear to influence the amount of acidic products liberated (Table 3). The type II kerogens (Kimmeridge and Monterey) produced by far the greatest concentration of acids. Interestingly both of the type I kerogens and the type II/III kerogen produced significantly lower amounts (Table 1).

Type III kerogens are characterized by generally having higher atomic O/C ratios than other kerogens and thus would be expected to generate the largest amounts of organic acids (Cooles *et al.*, 1987). The fact that the New Albany kerogen (Type II/III) was the most mature of the samples studied (Ro = 0.47%, Table 1) may explain the

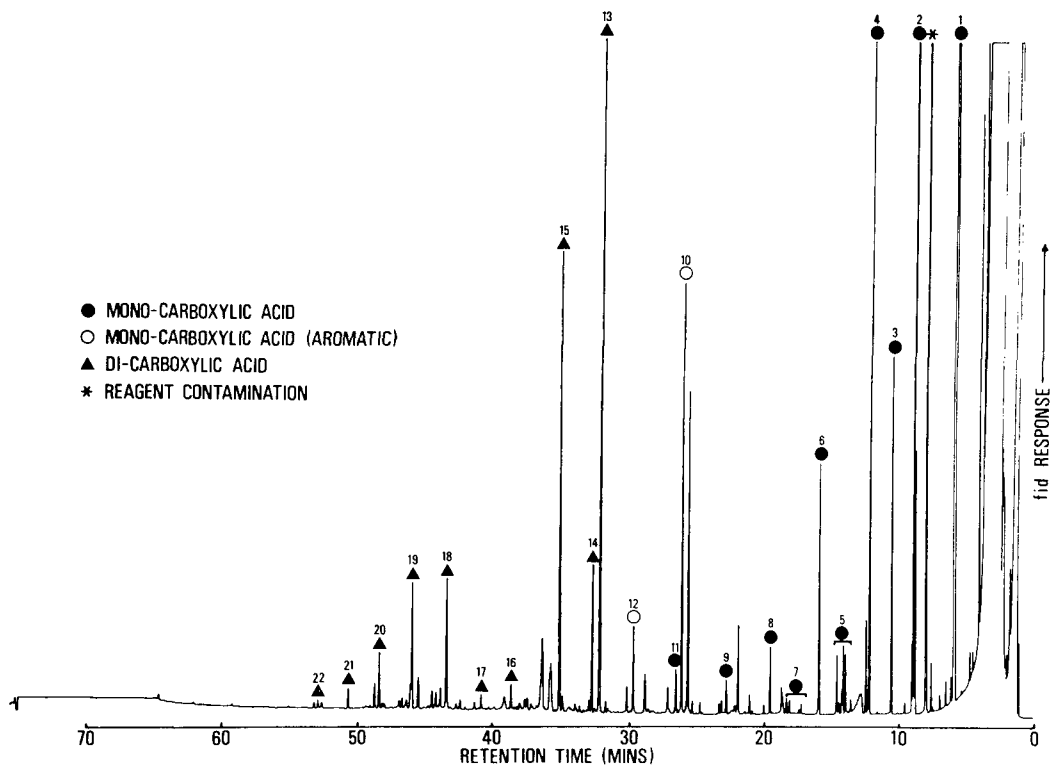


Fig. 1. Gas chromatogram showing a typical distribution of fatty acids (as *n*-butyl esters) in the aqueous products of hydrous pyrolysis of Kimmeridge kerogen. Sample: Kerogen + limonite, heated at 250°C for 720 hr. For peak assignments see Table 2.

lower acid yields since this kerogen may have already undergone substantial de-carboxylation.

Variations were also apparent within the distributions of acids released from the different kerogens. In the Kimmeridge sample, both mono- and di-carboxylic acids were present in significant amounts, with the latter detectable up to C_9 . The Guttenberg and New Albany kerogens yielded only minor amounts of dicarboxylic acids whilst the Green River kerogen produced a prominent series of di-carboxylic acids ranging from C_8 to above C_{12} , but only minor amounts of mono-carboxylic acids. These variations in acid distribution probably reflect differences in kerogen structure as well as maturity.

Treatment of the unheated kerogens with 0.005M KOH releases low molecular weight acids which may be either bound or adsorbed onto the matrix (Kawamura *et al.*, 1986). Table 1 shows the yields of organic acids liberated in this way from the different kerogens studied. The amounts vary slightly from kerogen to kerogen but are generally low and in all cases account for less than

30% of the acids produced during hydrous pyrolysis. These results suggest that the majority of acids liberated during laboratory heating are not simply trapped within the kerogen structure, but are the result of kerogen oxidation.

The effect of different experimental heating times on the generation of acids from the Kimmeridge kerogen is shown in Figs. 3 and 4. Individual acid concentrations are given in Table 3. Thus at 250°C (Fig. 3) the concentration of total acids increased steadily from approximately 1 mg g^{-1} after 72 hr to nearly 5 mg g^{-1} after 720 hr. A similar increase was observed at 280°C but the increase was unexpectedly somewhat less (Fig. 3). At 330°C (Fig. 4) the acid concentration was high (4.44 mg g^{-1}) after only 7.2 hr and this increased to 7.16 mg g^{-1} after 168 hr. Therefore it appears that prolonged heating increases the amount of acids produced and that the highest experimental temperature used (330°C) results in the greatest production.

Since short-chain acids, such as acetic acid, are believed to be unstable at temperatures exceeding

TABLE 2. Carboxylic acids identified in the aqueous products from hydrous of Kimmeridge kerogen. For peak elution order see Fig. 1.

Peak No. ¹	Retention time (mins)	Assignment	Trivial Name	Abbreviated Name
<u>Monocarboxylic acids (●)</u>				
1	5.8	Ethanoic* ⁺	Acetic	C ₂ -mono
2	8.8	Propanoic* ⁺	Propionic	C ₃ -mono
3	10.4	2-Methylpropanoic ⁺	Isobutyric	brC ₄ -mono
4	12.0	Butanoic* ⁺	Butyric	C ₄ -mono
5	13.8	2-Methylbutanoic ⁺	Anteisovaleric	} brC ₅
	14.4	3-Methylbutanoic ⁺	Isovaleric	
6	15.3	Pentanoic* ⁺	Valeric	C ₅ -mono
7	17.3	2-Methylpentanoic ⁺	Methylpropylacetic	} brC ₆ -mono
	18.2	3-Methylpentanoic ⁺	Butylacetic	
		4-Methylpentanoic ⁺	Isocaproic	
8	19.5	Hexanoic* ⁺	Caproic	C ₆ -mono
9	22.7	Heptanoic* ⁺	<i>n</i> -Heptylic/Enanthic	C ₇ -mono
10	26.0	Benzenecarboxylic* ⁺	Benzoic	Bz-mono
11	26.4	Octanoic* ⁺	Caprylic	C ₈ -mono
12	29.5	Methylbenzoic ⁺	Toluic	Tl-mono
<u>Dicarboxylic acids (▲)</u>				
13	32.0	Butanedioic* ⁺	Succinic	C ₄ -di
14	32.5	Methylsuccinic ⁺	Pyrotartaric	brC ₅ -di
15	35.0	Pentanedioic* ⁺	Glutaric	C ₅ -di
16	38.5	Hexanedioic* ⁺	Adipic	C ₆ -di
17	40.7	Heptanedioic* ⁺	Pimelic	C ₇ -di
18	43.4	Octanedioic* ⁺	Suberic	C ₈ -di
19	45.9	Nonanedioic ⁺	Azelaic	C ₉ -di
20	48.3	Decanedioic ⁺	Sebacic	C ₁₀ -di
21	50.6	Undecanedioic ⁺	-	C ₁₁ -di
22	52.9	Dodecanedioic ⁺	-	C ₁₂ -di

* Identified by comparison of gas chromatographic retention time with authentic standards.

⁺ Identification by comparison with published mass spectra or by direct interpretation.

¹ Refers to peak annotation in Fig.1.

200 °C (Kharaka *et al.*, 1983), the rate of production of the acids in these experiments must exceed their rate of destruction. It can thus be assumed that yields of acids generated at these artificially high temperatures are underestimates for the total acid producing potential of the kerogen since in nature viable reservoirs rarely exist at sub-surface temperatures above 200 °C.

The concentrations of acids produced by heating Kimmeridge kerogen at 330 °C for 7.2 hr in the presence of various minerals are shown in Table 4. It is obvious that the presence of the minerals does indeed influence the amounts of acids produced. Of the minerals examined at this temperature, limonite has by far the greatest effect, leading to a three-fold increase in acid production. XRD analysis showed that no detectable

changes had occurred to the mineral phases as a result of hydrous pyrolysis. The reasons why minerals other than limonite should affect acid generation is unclear; however, one possible explanation is that the minerals in question act as a surface on which de-carboxylation can take place (Kawamura *et al.*, 1986). The role of limonite is much more obvious because of its potential to act as an oxidant. The effect of limonite is of particular interest because previously it has been suggested that the acid-producing potential of a kerogen is limited by its oxygen content (Bjorlykke, 1981). Clearly this is not necessarily the case.

Whilst limonite increases the total acid concentration, it also affects the distribution of individual acids. For instance, aromatic acids such as benzoic

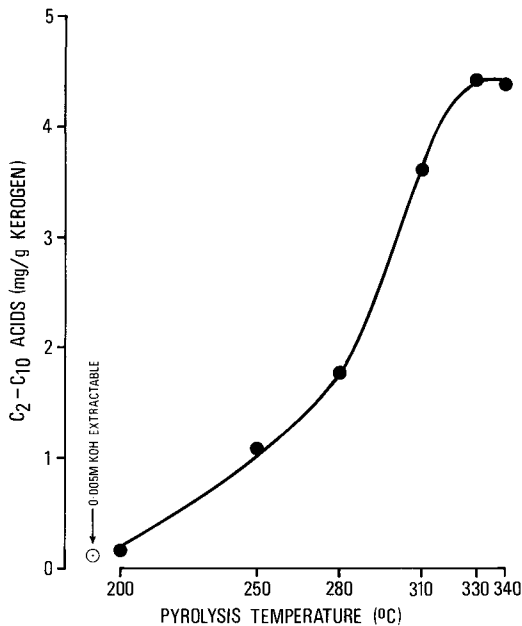


FIG. 2. Variation in total (C₂-C₁₀) acids released during hydrous pyrolysis of Kimmeridge kerogen at different temperatures for 72 hr.

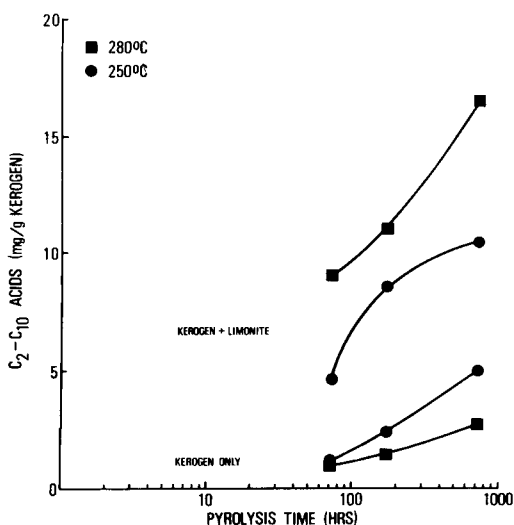
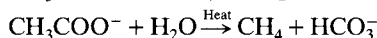
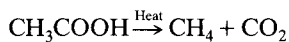


FIG. 3. Variation in the yield of total (C₂-C₁₀) organic acids released during hydrous pyrolysis of Kimmeridge kerogen at 250°C (circles) and 280°C (squares) in the presence and absence of limonite.

acid were only observed in significant quantities when the kerogen was heated with the mineral present. In general, both mono- and di-carboxylic acids were produced in increased abundance and as a result di-carboxylic acids were detected up to C₁₄.

The results of heating Kimmeridge kerogen for longer periods in the presence of limonite (168 hr, 720 hr) are also shown in Figs. 3 and 4. As with the 'kerogen-only' experiments, acid production is increased by prolonged heating at 250°C and 280°C (Fig. 3). At the highest temperature employed (330°C) a maximum in acid production (18.57 mg g⁻¹) was observed after 72 hr (Fig. 4) in which nearly 2% of the original kerogen is represented by the measured acids. However, prolonged heating (168 hr) at this high temperature in the presence of limonite led to a rapid depletion in acid generation. This is attributed to thermal decarboxylation of the acids by one of two mechanisms:



In a separate experiment where Kimmeridge kerogen was heated (hydrous pyrolysis, 330°C, 72 hr) with a 20-fold excess of elemental sulphur (Eglinton, unpublished results) elevated C₂-C₁₀ acid concentrations were also recorded (14.58 mg g⁻¹); however of greatest interest was the fact that benzoic acid accounted for almost 99% of the total acids.

As has been pointed out previously (Cooles *et al.*, 1987; Rowland *et al.*, 1986) care must be taken when comparing the results of experimental maturation studies (high temperatures, short-time) with natural geological heating processes (low temperatures, long-time). However, the similarities in overall distributions of the acids produced experimentally with those found in reservoir formation waters (notably a high abundance of acetic acid; Carothers and Kharaka, 1978) suggest that similar mechanisms are operating in both systems. Thus the results from the present experiments do suggest that kerogens are indeed a potential source of organic acids, especially in the presence of mineral oxidants. The geological significance of these results can only be assessed when mass balance calculations are made in order to determine the effects of up to 18.57 mg g⁻¹ of acids on sandstone mineral dissolution. Such calculations must take into account the subsequent migrational history of the acidic solutions and this is the subject of continuing research (Curtis, 1983).

Table 3. Concentration of C₂-C₁₀ organic acids liberated during hydrothermal pyrolysis of Kimmerridge kerogen (a) in the presence of water and limonite, (b) in the presence of water only; (c) in the presence of water and limonite.

Pyrolysis conditions		Mono-carboxylic acids (μg q ⁻¹)						Di-carboxylic acids (μg q ⁻¹)						Total acids (mg q ⁻¹)								
Temp (°C)	Time (hrs)	C ₂	C ₃	br-C ₄	C ₅	br-C ₆	C ₆	C ₇	C ₈	Bz	Tl	C ₄	C ₅	br-C ₆	C ₆	C ₇	C ₈	C ₉	C ₁₀	Total Mono	Total Di	Total Acids
(a) Kerogen + H ₂ O only																						
250	72	518	72	10	29	-	-	-	-	-	-	162	56	19	17	13	14	17	-	0.70	0.39	1.09
	168	1219	359	438	277	Tr	Tr	20	-	Tr	-	103	47	77	Tr	14	39	Tr	-	2.26	0.24	2.54
	720	2749	719	369	299	Tr	Tr	25	-	Tr	-	159	62	141	-	14	187	39	Tr	4.16	0.60	4.75
280	72	956	204	14	61	Tr	Tr	17	-	-	-	227	71	124	27	28	22	19	8	1.26	0.53	1.79
	168	1671	317	381	111	Tr	Tr	13	-	-	-	177	57	127	-	-	77	Tr	-	1.77	0.77	2.54
	720	1666	381	22	107	Tr	Tr	23	-	-	-	113	38	99	-	-	59	51	Tr	2.18	0.36	2.54
330	7+2	2825	701	206	253	Tr	34	-	5	Tr	-	170	67	91	13	36	27	18	Tr	4.03	0.41	4.44
	72	3180	411	310	190	36	11	-	-	-	-	79	22	94	-	-	57	28	-	4.13	0.28	4.41
	168	4657	1351	316	505	28	103	-	-	-	-	54	19	45	-	-	45	20	Tr	6.98	0.18	7.15
(b) Kerogen + Limonite																						
250	72	3269	441	54	133	37	60	16	17	-	51	247	44	89	-	11	47	99	15	4.14	0.42	4.53
	168	6077	981	135	767	63	118	38	34	36	129	539	66	229	-	-	99	52	38	7.93	1.02	8.95
	720	7560	1405	141	339	65	105	7	33	15	194	43	360	62	272	-	116	99	40	9.21	0.90	10.51
280	72	6466	1087	256	396	62	134	25	69	Tr	109	276	38	157	14	15	129	87	43	8.63	0.73	9.35
	168	1677	3555	527	327	89	209	62	124	34	110	46	213	25	113	-	83	83	57	11.02	0.46	11.56
	720	10825	3188	362	1034	190	433	103	242	94	36	194	Tr	170	-	-	148	94	56	16.74	0.16	16.94
330	7+2	8613	2072	370	745	132	292	73	171	77	175	49	186	21	190	-	147	99	55	12.77	0.70	13.47
	72	11908	3559	501	1234	199	480	99	251	87	23	59	17	Tr	33	Tr	62	44	Tr	18.41	0.16	18.57
	168	500	72	-	12	-	-	-	-	-	-	20	-	-	-	-	15	-	Tr	0.58	0.03	0.61

(Tr, Trace; -, absent)

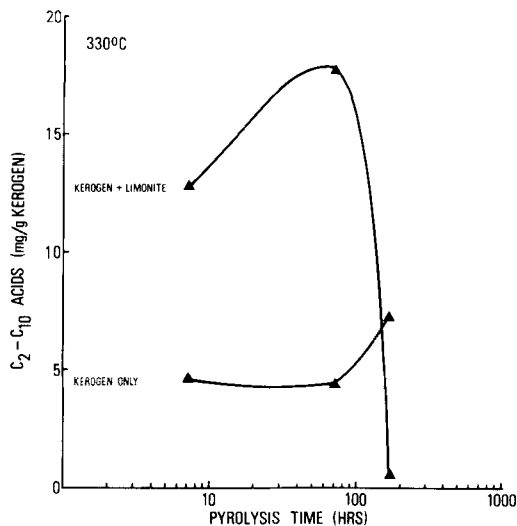


FIG. 4. Variation in the yield of total (C_2-C_{10}) organic acids released during hydrous pyrolysis of Kimmeridge kerogen at 330 °C, in the presence and absence of limonite.

TABLE 4. Effect of mineralogy on water-soluble acid yield during hydrous pyrolysis (300 °C, 7.2 hr) of Kimmeridge kerogen.

MINERAL	C_2-C_{10} ACIDS (mg/g KEROGEN)		
	MONO-CARBOXYLIC	DI-CARBOXYLIC	TOTAL
Kerogen only	4.03	0.41	4.44
Kerogen + Kaolinite	3.02	0.65	3.67
Kerogen + $CaCO_3$	5.90	0.33	6.23
Kerogen + Limonite	12.77	0.70	13.47

Conclusions

Hydrous pyrolysis of kerogens generates significant amounts of water-soluble organic acids. The amount and distribution of C_2-C_{10} acids varies with kerogen type and maturity.

Yields of organic acids are substantially enhanced when Kimmeridge kerogen was artificially matured in the presence of limonite and under the most favourable experimental conditions employed (kerogen and limonite, 330 °C, 72 hr) total water-soluble acids account for almost 2% of the original kerogen. This result suggests

that the acid-producing potential of a kerogen may not be limited by its oxygen content.

The quantitative significance of low molecular weight organic acids liberated from kerogens, in terms of their ability to affect mineral stability, is difficult to assess. Straightforward mass balance calculations (based on the kerogen content of a shale, its acid-producing potential and the mass of the adjacent sandstone body) are complicated by a number of factors. These include the extent to which acidic solutions would be neutralized as a result of complexing with metals in the host-shale, the mode of expulsion, and, of course, the fact that the acid-producing potential has been determined indirectly through artificial maturation experiments. Nevertheless the results of this preliminary study suggest that kerogen may be an important source of organic acids.

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