Long-chain aliphatic nitriles in pyrolysates of young kerogen: implications for the intermediates in petroleum hydrocarbon formation

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Gas chromatographic/mass spectrometric examination of products from laboratory thermal degradation of kerogen from a young marine sediment (Tanner Basin off California), revealed a series of long-chain nitriles whose carbon-chain lengths range from 12 to 26. These compounds appeared after the relatively mild thermal conditions of 310-350°C for 5-116 hrs and disappeared before major n-alkane generation. We hypothesise that n-alkanes are generated at the expense of long-chain fatty nitriles which in turn are formed via fatty acid amide-linked structures in kerogen.

Heating of standard long chain (C18) fatty acid amides with kerogen produced n-alkanes with no odd/even predominance. The heating experiments showed that these nitrogen compounds have a strong potential for producing a series of normal hydrocarbons. Consequently, nitrogen-linked long-methylene-chain structures in kerogen analogous to fatty acid amides/fatty nitriles can act as one of the precursors of petroleum hydrocarbons.

INTRODUCTION

Petroleum genesis has long been one of the subjects of extensive research in geochemistry. Although kerogen has been accepted by many workers as a precursor of n-alkanes in petroleum and numerous studies have been conducted in support of this idea (Tissot and Welte 1984), questions have remained unanswered as to how n-alkyl chains are linked to kerogen during its formation and on what types of chemical reactions are involved in n-alkane generation from kerogen.

We have conducted artificial maturation (laboratory heating) experiments of young kerogens as an approach to solving these problems. This type of experiment is one of the more useful approaches to elucidating the chemistry of petroleum genesis, although it has been often criticized because of its completely different time-temperature relationship as compared with geological processes (Durand 1983; Ishiwatari et al. 1976, 1977; Ishiwatari and Fukushima 1979; Saxby et al. 1986; Saxby and Riley 1984; Tegelaar et al. 1989).

During a GC/MS (gas chromatography/mass spectrometry) survey of organic compounds with polymethylene chains in the thermal alteration products of a young kerogen, organonitrogen compounds including straight-chain fatty nitriles were found in the benzene fraction of pyrolysis bitumens (moderately polar pyrolysates). The presence of organonitrogen compounds (pyridines, quinolines, benzoquinolines, carbazoles etc.) in crude oils has been reported by a number of authors (reviewed by Bakel and Philp 1990) and discussed in terms of their role as indicators of depositional environments and maturity.

We report here the analytical results on nitrogen-containing products of laboratory thermal alteration of a young kerogen with discus-
sion of a role of these compounds as one of the precursors in petroleum hydrocarbon formation.

**EXPERIMENTAL**

*Materials and experimental procedures*

The organic matter from a recent marine sediment of Tanner Basin, offshore California, was concentrated by HF/HCl dissolution of mineral matter. Tanner Basin is well-known as one of the sedimentary environments thought to be similar to sedimentary environments from which most of California's oil in the Late Tertiary was produced (Gorsline et al. 1968).

The organic matter was freed of lipid to recover kerogen by Soxhlet-extraction with benzene/methanol (6:4) prior to use for this heating experiment. Approximately 0.3 g of powdered kerogen was taken in a Pyrex glass tube (25 mm o.d. × 250 mm), sealed under nitrogen gas and heated at a single temperature between 200 and 370°C for different times ranging from 5 to 116 hrs. After the glass tube was opened, kerogen was extracted with benzene/methanol (6:4) by sonication. The benzene/methanol extract was separated by silica gel column chromatography into four fractions: (1) saturated aliphatic hydrocarbons (n-hexane eluate), (2) unsaturated and aromatic hydrocarbons (n-hexane eluate), (3) moderately polar compounds (benzene eluate) and (4) polar compounds (benzene/methanol eluate). The fractions were concentrated to near dryness, dissolved and analyzed by GC/MS.

*GC/MS analysis*

The GC/MS analyses were carried out with a Finnigan INCOS-50 quadrupole mass spectrometer connected with a Varian 3400 GC instrument. The chromatographic conditions were as follows: temperature was programmed from 60 to 120°C at 10°C/min, from 120 to 310°C at 5°C/min, and then held isothermal at 310°C for 20 min. Helium was used as carrier gas. The mass spectrometric data were acquired in the electron impact (EI) mode at 70 eV, scanning from m/z 50 to 650 at 1.5 sec per scan.

**RESULTS**

The analytical results for the first two fractions (n-hexane eluates), which have been already reported, indicated that the heating experiment mimics essentially natural process of generation of petroleum hydrocarbons (Ishiwatari et al. 1977; Ishiwatari and Fukushima 1979). Bitumen (organic solvent-soluble fraction) is generated from kerogen upon heating, its amount increasing sharply with increasing heating temperature from 250 to 300°C, that is, with increasing artificial kerogen maturity. Bitumen generation reaches a maximum when the atomic H/C ratio of kerogen is 0.90 to 0.95 and drops with decreasing H/C ratio. In contrast, n-alkanes begin to be generated around a kerogen H/C ratio of 1.1, reaching a maximum around H/C = 0.8 and then decreasing, as shown in the last two columns in Table 1.

*Generation of nitrogen-linked long-methylene-chain compounds on heating*

Figure 1 shows a typical gas chromatogram (reconstructed ion chromatogram) of the benzene fraction (moderately polar) obtained after heating the kerogen at 350°C for 10 hrs. A series of peaks are seen on the gas chromatogram. These peaks gave EI mass spectra typical of fatty nitriles, i.e., characterized by a base peak at m/z = 97 and fragment ions with even mass numbers of 110, 124, 138, 152 etc; molecular ions are not apparent. Figure 2 gives a mass spectrum of a representative component (peak A in Fig. 1), which was identified to be n-C_{16} fatty nitrile. In order to assess the molecular weights of these compounds, CI mass spectra using iso-butane as a reagent gas were obtained. The CI mass spectra revealed the intense ions, corresponding to [M+1] of saturated fatty nitriles whose carbon-chain length ranges from 12 to 26. From comparison of GC retention times with those of standards (n-C_{17} and n-C_{18} fatty nitriles) and the regularities of GC retention times, these peaks are concluded to be
Fig. 1. Reconstructed ion chromatogram of a benzene fraction (moderately polar compounds) of pyrobitumen produced by heating a young kerogen (Tanner Basin) at 350°C for 10 hrs. Cn indicates carbon number of normal fatty nitriles. Peak A: identified as n-C\textsubscript{16} fatty nitrile (See Fig. 2).

Fig. 2. Mass spectrum of a pyrolysis product (peak A in Fig. 1) identified as n-C\textsubscript{16} fatty nitrile.
straight-chain fatty nitriles.

The compounds generated by heating at lower temperatures show a preference for even carbon number, being quite similar to the distribution of fatty acids in marine sediments, suggesting a close genetic relation between fatty acids and fatty nitriles.

**Generation of carbazoles and benzoquinolines**

When heating under the conditions of larger thermal stress (at higher temperatures or for longer period), fatty nitriles in these fractions became minor while carbazoles became dominant (Table 1). Figure 3 shows a gas chromatogram (reconstructed ion chromatogram) of the benzene fraction obtained by heating at 350°C for 100 hrs. Mass chromatograms obtained by monitoring the molecular ions of carbazole and alkylated carbazoles showed a series of these compounds (alkyl: C₆-C₄), as given in Fig. 4. Figure 5 gives a mass spectrum of the peak which was identified as carbazole. The mass spectrum gives a base peak at m/z = 167, which is the molecular weight of carbazole. The alkylated carbazoles generally give a base peak corresponding to the molecular ions. Mass chromatograms obtained by monitoring the molecular ions of benzoquinoline and alkyl-substituted benzoquinolines show the presence of these compounds (alkyl: C₀-C₄) in the benzene fraction, as shown in Fig. 6. Mass spectra of these compounds give a base peak at their molecular weight and a fragment representing a loss of [H + CHN] (m/z = 28), which are similar to published mass spectra (Bakel and Philp, 1990).

Carbazoles, alkyl-substituted carbazoles, benzoquinolines and alkyl-substituted benzoquinolines are present in crude oils and pyrolysates of fossil kerogens (e.g. Bakel and Philp 1990). Moreover, the detection of these compounds in the pyrolysates of our young kerogen at higher thermal stress is consistent
Fig. 4. Reconstructed ion chromatogram and mass chromatograms obtained by monitoring the molecular ions for carbazole and alkylated carbazoles. Pyrolysate from heating kerogen at 350°C for 100 hrs.

Fig. 5. Mass spectrum of a pyrolysis product (peak B in Fig. 3) identified as carbazole.
Fig. 6. Reconstructed ion chromatogram and mass chromatograms obtained by monitoring the molecular ions for benzoquinoline and alkylated benzoquinolines. Pyrolysate from heating kerogen at 350°C for 100 hrs.

Table 1. Approximate composition of degradation products (moderately polar compounds) at different thermal conditions

<table>
<thead>
<tr>
<th>Sample no</th>
<th>Condition of Heating</th>
<th>Composition of Products</th>
<th>n-Alkanes (C_{17}-C_{31}) (µg/g-kerogen)</th>
<th>Atomic H/C of kerogen after heating</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature (°C)</td>
<td>Duration (hr)</td>
<td>Nitriles (µg/g-kerogen)</td>
<td>Carbazoles (µg/g-kerogen)</td>
</tr>
<tr>
<td>K-29</td>
<td>310</td>
<td>5</td>
<td>4</td>
<td>210</td>
</tr>
<tr>
<td>K-32</td>
<td>310</td>
<td>20</td>
<td>ND</td>
<td>670</td>
</tr>
<tr>
<td>K-4</td>
<td>310</td>
<td>24</td>
<td>470</td>
<td>540</td>
</tr>
<tr>
<td>K-31</td>
<td>310</td>
<td>66</td>
<td>170</td>
<td>1210</td>
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<td>K-30</td>
<td>310</td>
<td>116</td>
<td>170</td>
<td>1180</td>
</tr>
<tr>
<td>K-15</td>
<td>350</td>
<td>5</td>
<td>130</td>
<td>370</td>
</tr>
<tr>
<td>K-12</td>
<td>350</td>
<td>10</td>
<td>430</td>
<td>tr</td>
</tr>
<tr>
<td>K-9</td>
<td>350</td>
<td>18</td>
<td>tr</td>
<td>*</td>
</tr>
<tr>
<td>K-11</td>
<td>350</td>
<td>35</td>
<td>tr</td>
<td>****</td>
</tr>
<tr>
<td>K-14</td>
<td>350</td>
<td>60</td>
<td>*</td>
<td>620</td>
</tr>
<tr>
<td>K-13</td>
<td>350</td>
<td>100</td>
<td>tr</td>
<td>***</td>
</tr>
</tbody>
</table>

***abundant; ** intermediate; * poor; tr trace

with a result obtained by Bakel and Philp (1990), where benzoquinolines and carbazoles are dominant in the pyrolysates of Phosphoria Formation rock samples at high heating temperatures (350°C). These results indicate that the thermal processes regulating the generation of nitrogen-containing compounds in our heating experiment are essentially the same as those in a model heating experiment of natural maturation of the Phosphoria shale.

Precursor materials of these compounds have been discussed by several authors (Schmit-
Long-chain aliphatic nitriles

Schmitter and Arpino (1983) claimed that ring enclosure by reaction of ammonia or amines trapped in kerogen with sites analogous to 1,5-dioxo derivatives is one of the possible processes for producing these nitrogen-containing compounds. Bakel and Philp (1990) pointed out the possibility of incorporation of peptide nitrogen into the kerogen matrix during diagenesis.

In our heating experiment, carbazoles and benzoquinolines are not detected at low thermal stress, as shown in Table 1. This indicates that these compounds are formed from nitrogen-containing precursors at high thermal stress and are thermally stable.

**DISCUSSION**

*Fatty nitrile and n-alkane relation by heating experiments using standards of fatty nitrile and fatty acid amide*

Fatty nitriles were quantified by GC using standard n-C18 nitrile (purity 90+%, Aldrich Chemical Co.) as an external standard. Table 1 summarizes the result of GC analysis of the benzene fractions obtained at different heating temperatures and times.

As shown in Table 1, the fatty nitrile generation reaches a maximum in the heating at 310°C for 24 hrs (# K-4) or 350°C for 10 hrs (# K-12) and then decreases with increasing heating time. It is clear that fatty nitriles are generated at relatively milder thermal conditions than that for the intensive n-alkane generation where the generation of the nitriles are almost nil.

The difference in the amounts of fatty nitriles between the maximum generation of fatty nitriles and that of n-alkanes, is roughly $-300 \mu g/g$-kerogen for the heating at 310°C and $-430 \mu g/g$-kerogen at 350°C, while the differences in the amounts of n-alkanes between the maximum generation of fatty nitriles and that of n-alkanes is $+660 \mu g/g$-kerogen and $+300 \mu g/g$-kerogen respectively; as shown in Table 2. Thus, the decrement of fatty nitriles almost correspond to the increment of n-alkanes.

It was hypothesized from the above results of fatty nitriles on heating that there is a route of n-alkane generation via nitrogen-containing compounds and/or structures (e.g. fatty nitriles and/or related structures in kerogen), in addition to the generally considered route irrelevant to nitrogen (e.g. Tissot and Welte 1984).

The following experiment was carried out to test the ability of fatty nitriles for producing n-alkanes. The standard n-C18 fatty nitrile (purity 90+%) was heated with a young kerogen (Tan- ner Basin kerogen) in a Pyrex glass tube filled with nitrogen gas at 340°C for 48 hrs, and examined for n-alkane. The weight ratio of the C18 fatty nitrile to kerogen was arbitrarily set at about

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Condition of Heating</th>
<th>Fatty Nitriles ($\mu g/g$-kerogen)</th>
<th>n-Alkanes ($\mu g/g$-kerogen)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K-4</td>
<td>310 24</td>
<td>470</td>
<td>540</td>
</tr>
<tr>
<td>K-31; K-30</td>
<td>310 66; 116</td>
<td>170</td>
<td>1200±20</td>
</tr>
<tr>
<td>Difference: (2)-(1)</td>
<td></td>
<td>-300</td>
<td>+660</td>
</tr>
<tr>
<td>K-12</td>
<td>350 10</td>
<td>430</td>
<td>990</td>
</tr>
<tr>
<td>350 18; 35</td>
<td>0</td>
<td>1290±130</td>
<td></td>
</tr>
<tr>
<td>Difference: (2)-(1)</td>
<td></td>
<td>-430</td>
<td>+300</td>
</tr>
</tbody>
</table>
Fig. 7. Molecular composition of normal alkanes/alkenes generated from standard normal C\textsubscript{18} fatty nitrile or C\textsubscript{18} fatty acid amide on heating. (A) standard compound (5 mg) was heated with kerogen (15 mg) in a Pyrex glass tube at 340°C for 48 hrs; (B) standard compound was heated alone at 340°C for 48 hrs.

1:4 (5 mg nitrile vs. 18 to 19 mg kerogen). When the C\textsubscript{18} fatty nitrile-kerogen mixture was heated, a series of normal C\textsubscript{13}-C\textsubscript{17} hydrocarbons were generated as shown in Fig. 7 (A: left). The amount of individual hydrocarbons generated from the fatty nitrile-kerogen mixture, was corrected for the amount obtained from a blank experiment (the kerogen was heated alone). The blank experiment was heated at 340°C for 48 hrs under the similar heating condition to that of the fatty nitrile-kerogen mixture, and produced a negligibly small amount of n-alkanes (less than 1% of the n-alkanes generated from the heating of the fatty nitrile-kerogen mixture), and no n-alkenes were generated.

The hydrocarbons generated from the fatty nitrile-kerogen mixture are essentially composed of n-alkanes and n-alkenes, the former being the more abundant. The n-C\textsubscript{17} alkane is the most abundant. Normal C\textsubscript{13}-C\textsubscript{16} alkanes are also present and show no odd/even predominance. n-Alkenes of C\textsubscript{13}-C\textsubscript{17} are minor components.

The precursor of the fatty nitriles generated from the kerogen was thought to be (1) fatty acid (FA) amides which might be trapped in the kerogen structure and/or (2) FA amide-derived structure of unknown N-linkage. Therefore, an ability of FA amides for generating n-alkanes was tested by heating standard n-C\textsubscript{18} FA amide (purity 90+%; Aldrich Chemical Co.) with the Tanner Basin kerogen at 340°C under the same conditions used for heating the C\textsubscript{18} fatty nitrile with the kerogen. As shown in Fig. 7 (B: right), the heating experiment gave essentially the same result as that for the C\textsubscript{18} fatty nitrile, where n-C\textsubscript{17} alkane was predominant. The yield of n-alkanes from FA amide was about twice that obtained from the fatty nitrile.

The experimental results described above clearly indicates that both FA amides and fatty nitriles can produce n-alkanes and that the yield of n-alkanes is higher compared with n-alkenes.
Therefore, FA amides and fatty nitriles may act as one of the precursors of petroleum hydrocarbons, although the approximate yields of n-alkanes from the fatty nitrile or the FA amide are low, ranging from 5 to 10%.

To clarify the role of the kerogen matrix in generation of n-alkanes from FA amides and fatty nitriles, the n-C\textsubscript{18} FA amide or the n-C\textsubscript{18} fatty nitrile was heated alone at 340°C for 48 hrs and the results were compared with those obtained for heating in the presence of kerogen. Heating of the both compounds alone produced a considerably larger amount of n-alkenes than n-alkanes, as shown in Fig. 7(B). This result is markedly different from heating these compounds in the presence of kerogen (Fig. 7(A)). It is obvious, therefore, that kerogen plays an important role in the generation of n-alkanes from fatty nitriles/FA amides probably as acting acid catalyst, which will be discussed in detail elsewhere.

**Possibility of a pathway of petroleum hydrocarbon formation via organo-nitrogen structures in nature**

According to one of the current ideas (Kissin 1987), n-alkanes in petroleum are generated by thermocracking of the heavy n-alkanes which are generated by decarboxylation of living organisms-derived fatty acids or esters. Isoalkanes are formed from alk-1-enes in the presence of acidic clays. Tegelaar et al. (1989) have proposed a route in the generation of n-alkanes in high-wax oils via thermocracking of insoluble non-hydrolyzable aliphatic biopolymers.

Although evidence is limited, the following three-stage pathway via nitrogen-containing intermediates can be proposed as an additional possible process of generating petroleum hydrocarbons. Fatty acids and ammonia are trapped in kerogen at relatively early stages of diagenesis (Stage 1). These compounds react with each other and produce fatty acid amides and/or are incorporated into kerogen structure via N-C linkage (Stage 2). At later stages of diagenesis, petroleum hydrocarbons are generated by cleavage of N-C linkages (Stage 3).

Our hypothesis requires more testing before it can be accepted. The test includes the elucidation of the existence and chemical forms of nitrogen-linked long methylene-chain structures in kerogen and sediments. Our hypothesis predicts the presence of FA amides and/or fatty nitriles in sediments and sedimentary rocks at early to middle stages of diagenesis, and also predicts the presence of nitrogen-linked long-chain structure in kerogen analogous to fatty acid amides/fatty nitriles at different evolution stages.

**CONCLUSION**

1. Three types of nitrogen-containing compounds, long-chain fatty nitriles, carbazoles and benzoquinolines are found in the pyrolysates of kerogen from a young marine sediment.

2. Long-chain fatty nitriles appear at early stages of pyrolysis (5 to 116 hrs at 310°C and 5 to 18 hrs at 350°C), whereas carbazoles and benzoquinolines appear at late stages (18 to 100 hrs at 350°C).

3. A hypothesis of generation of n-alkanes at the expense of long-chain fatty nitriles is proposed from the pyrolytic behavior of fatty nitriles (C\textsubscript{12}–C\textsubscript{26}).

4. A heating experiment of standard long-chain (C\textsubscript{18}) fatty acid amides or fatty nitriles with kerogen shows that these nitrogen compounds have the potential for producing n-alkanes.

5. Nitrogen-linked long-methylene-chain structure in kerogen analogous to fatty acid amides/fatty nitriles can be one of the precursors of petroleum hydrocarbons.

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**REFERENCES**


