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Photo-oxidation of 1-methylnaphthalene dissolved in seawater and exposed to sunlight under quasi-environmental conditions

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Abstract

Solutions of 1-methylnaphthalene in membrane-filtered natural seawater were exposed to sunlight in quartz vessels. The same solutions in amber glass vessels served as a dark control. Photo-oxidation products identified were: 1-naphthaldehyde, 1-hydroxymethylnaphthalene, 3-methyl-1(3*H*)-isobenzofuranone, glyoxal, and traces of 4-methyl- and 7-methyl-1(3*H*)-isobenzofuranone, these last two compounds being tentatively identified on the basis of their mass spectra. The products with an unchanged carbon skeleton suggest sensitizer-mediated hydrogen abstraction. The reaction sequence leading to the formation of glyoxal and the isobenzofuranones is proposed as starting with the addition of singlet molecular oxygen to the aromatic double bond system.

After 10 days of exposure to summer sunlight at Kiel, Germany (54° 20′ N), the concentration of 1-methylnaphthalene decreased to approximately 50% of the initial value, whereas the concentration in the dark control remained essentially unchanged. The intensities of impinging solar UVA and UVB radiation were recorded to enable the extension of the observed photo-oxidation rate to light regimes deviating from those of the experiment. © 1997 Elsevier Science S.A.

Keywords: Dissolved oil components; Alkylnaphthalenes; Photooxidation; Ring fragmentation; Mass spectrometry

1. Introduction

Alkylnaphthalenes are common crude oil constituents [1] with relatively high solubilities in water. It is not surprising, therefore, that many members of this group of compounds have been found as major or principal components of aromatic hydrocarbon fractions recovered from sea areas chronically or accidentally contaminated with petroleum and/or its distillates [2–4]. 1-Methylnaphthalene (1-MN) was selected as model compound to study the photo-oxidation reactions of this group of compounds by chemical product characterization. To mimic environmental conditions in a spill situation as closely as possible, a dilute solution of 1-MN in seawater without added sensitizers was exposed to natural sunlight in a UV transparent flask made of vitreous silica. Before being used as reaction medium, coastal Baltic Sea water, which is eutrophic and rich in micro-organisms, was passed through glass fibre and membrane filters to reduce the concentration of microorganisms. These were expected rapidly to degrade 1-MN and thus to mask the effects of photo-oxidation, which may be an important removal mechanism in oligotrophic water masses exposed to intense solar radiation at low latitudes.

To asses the effects of degradation by micro-organisms which might have passed through the filters or which could contaminate the water by accidental introduction during sampling, the same solution of 1-MN protected against actinic radiation by enclosure in an amber glass vessel was exposed simultaneously and for an identical period of time.

The reduced number of carbon atoms in the skeleton of some photo-oxidation products implied that compounds had been generated which were missed by the analytical protocol initially selected for the experiment. In attempts to characterize these compounds, the experiment was repeated twice under slightly different weather conditions. With respect to photo-oxidation products identified in the first experiment the results were qualitatively similar, although different light regimes affected the rate of photo-oxidation.

2. Experimental procedures

1-Methylnaphthalene and 2-methylnaphthalene (both Merck commercial reagents) were vacuum-distilled under

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nitrogen and checked for purity by gas chromatography before use. Solvents (n-hexane, dichloromethane, methanol and acetonitrile) were purified by fractionated distillation through 1.5 m vacuum-jacketed and silver-plated columns filled with glass helices; the reflux ratio was 1:20. Periodic checks were made for impurities by GC/MS analyses of 1000-fold concentrates.

The seawater used for the experiments was sampled at the wharf of the Institut für Meereskunde in Kiel from a depth of approximately 1 m. A submersible gear pump forced the water through a glass fibre filter (GF/F equivalent Schleicher & Schüll GF 6, pre-heated for 24 h at 400 °C to remove organic impurities) and a 0.1 μm cellulose nitrate membrane filter (Sartorius) into a steam-sterilized glass carboy of 10 l capacity (both filters were 14 cm in diameter). The filtration was repeated by gravity flow through a stainless steel filter holder which had been steam-sterilized, with the same filter combination. The water was collected under sterile conditions in a 4 l three-neck round bottom flask equipped with a cotton wool-protected air inlet, a septum, and a base drain. 1-Methylnaphthalene was added through the septum and the water was stirred slowly on a magnetic stirrer overnight.

The seawater solution of 1-MN was drained under sterile conditions from the equilibration flask into a quartz vessel (capacity 1.5 l) and a vessel of equal size and shape made of amber Pyrex glass. For an experiment, the vessels were placed in cradles next to each other and exposed to natural sunlight on the flat roof of the Institute building at Kiel (54° 20′ N). To monitor changes in concentrations, the solutions were sampled daily with sterilized all-glass hypodermic syringes. The air replacing the withdrawn water had to pass through plugs of cotton wool to maintain the sterility of the remaining water. Microbial counts were checked in the samples, to which was added immediately after sampling 40% aqueous formaldehyde so that its final concentration was 0.8%. After staining with acridine orange, cells were counted with an epifluorescence microscope.

To determine concentrations of 1-MN, 4.0 μl internal standard solution (4.99 μg 2-methylnaphthalene per μl acetonitrile) were added to 1.00 ml sample water in a 2.0 ml glass ampoule with a crimped-on septum cap. Analyte and internal standard were sampled from the aqueous solution by concentration with a solid phase micro-extractor (SPME, Supelco No. 5-7330) equipped with a 30 μm polydimethylsiloxane fibre assembly; equilibration time was 1 min. The substances were desorbed (30 s) in the hot injector (250 °C) of a Hewlett-Packard 5993 C GC/MS instrument equipped with a 25 m × 0.25 mm i.d. fused silica column chemically bonded with 95% dimethyl–5% phenylsilicone (Chrompack CP-Sil 8CB; equivalent phases: DB-5, SE-52, OV-73). During desorption the split valve remained closed. The initial oven temperature of 40 °C was held for 1 min, then ramped at 20 °C min^{-1} to 100 °C and further increased at 5 °C min^{-1} to 150 °C with 2 min hold time at T_{max}. Mass spectrometric data acquisition in scan mode started 3.7 min after sample desorption. Quantification was based on injections of external standards. Total (TIC) or molecular ion current (MIC) peak areas were integrated manually. For qualitative analyses the conditions were as follows: splitless injection (30 s) at 40 °C oven temperature (1 min), 20 °C min^{-1} to 60 °C, 5 °C min^{-1} to 300 °C, 5 min hold time at T_{max}.

During the first of three experiments, solar radiation intensities were measured with a UVA sensor (band width 315–380 nm) and a UVB sensor (band width 280–315 nm), both from Technetics Messwerterfassungssysteme GdbR, D-79115 Freiburg, Germany. The analogue signals from the sensors were recorded with a J.E.T. Mikromec digital data logger (Jessen Electronic Team, D-35335 Elmshorn, Germany).

Following the period of sunlight exposure, the water was extracted three times with n-hexane, and the hexane solutions were dried over anhydrous sodium sulphate, concentrated by rotary evaporation and separated into four fractions of increasing polarity by chromatography over activated silica gel. Each fraction was concentrated and analysed by GC/MS.

The mass spectra of some of the photo-oxidation products could be identified by computer-aided comparison with a mass spectral data base; other mass spectra had to be interpreted according to established rules. Most mass spectrometric identifications were verified by GC/MS comparison either with commercially available reference compounds or with compounds synthesized for that purpose.

The reduced number of carbon atoms in the structures of photo-oxidation products identified in the first experiment suggested the formation of low molecular weight volatile compounds as fragments. To search for non-polar volatiles, 400 ml samples were sparged with ultrapure helium for 15 min at room temperature at a flow rate of 100 ml min^{-1}. The gas was dried by passage through a small Liebig condenser held at −15 °C and through a short tube filled with calcium chloride before it entered a 3 mm i.d. glass tube filled with 0.2 g Supelco Carbosieve SIII to trap volatiles. A Tekmar Model 5010 Automatic Desorber was used to introduce desorbed material into a 30 m × 0.32 mm Supelco Carboxen 1006 PLOT column installed in the Hewlett-Packard 5993C GC/MS.

To screen for low molecular weight carbonyl compounds, the 1-MN photo-oxidation products were reacted with 2,4-dinitrophenylhydrazine at pH 1; the dinitrophenylhydrazones were extracted with dichloromethane. The solvent was evaporated below room temperature and the residue was dissolved in acetonitrile. The acetonitrile solution was analysed by HPLC on a Supelco Spherisorb ODS2 (5 μm) column. Elution was isocratic with 70% aqueous acetonitrile at a flow rate of 1.0 ml min^{-1}. The detection wavelength was 420 nm.

3. Results and discussion

3.1. Photo-oxidation products

Unreacted 1-MN (silica gel fractions 1 and 2) and traces of bis-(2-ethylhexyl) phthalate (silica gel fraction 4) were

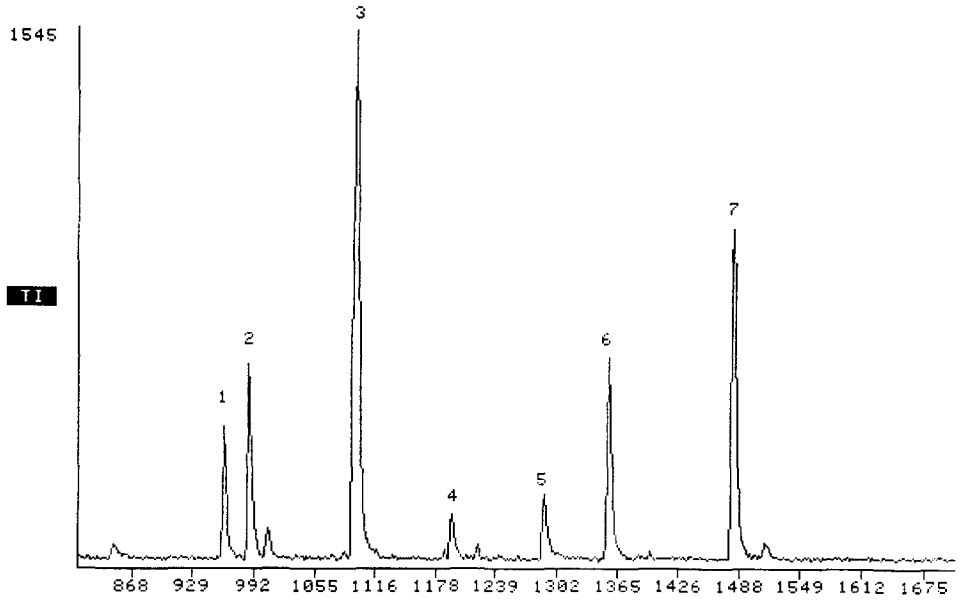

Fig. 1. Total ion chromatogram of combined fractions 3 and 4 of 1-methylnaphthalene photo-oxidation products.

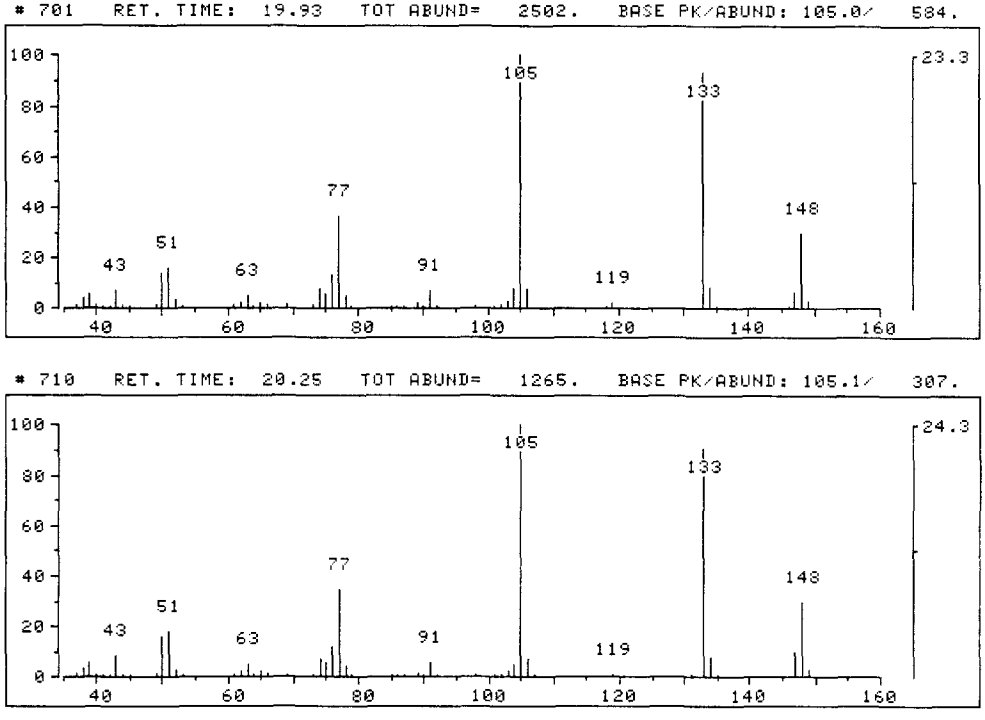

Fig. 2. EI mass spectra of the compound represented by peak 3 in Fig. 1 (top) and of synthetic 3-methyl-1(3*H*)-isobenzofuranone (bottom).

the only compounds recovered from the water in the amber Pyrex flasks. 1-MN was also the only compound found in fractions 1 and 2 of the water exposed to sunlight. Fractions 3 and 4 recovered from the sunlight-exposed water were eventually combined because of the small number of compounds in them. Fig. 1 shows the total ion chromatogram.

Peak 1 is the internal standard (2-MN). Peak 2 denotes an unidentified compound (mass spectrometric parent peak m/z 143; fragments m/z 128 (17.9%) and m/z 115 (18.3%)). The compounds represented by peaks 6 and 7 in the TI chromatogram were identified by comparison of their mass spectra and gas chromatographic retention indices with those of authentic reference compounds as 1-naphthaldehyde and 1-hydroxymethylnaphthalene. The mass spectrum corresponding to the intense peak is shown in the upper half of Fig. 2; no match could be found for it in mass spectral libraries. The difference of 15 mass units between the parent peak at m/z 148 and that at m/z 133 indicates loss of a methyl group. The differences of 28 mass units each from m/z 133 to m/z 105 and from m/z 105 to m/z 77, together with the peak at m/z 51, suggested consecutive loss of two carbonyl groups from a benzene ring. Mindful of the structure of the starting mate-

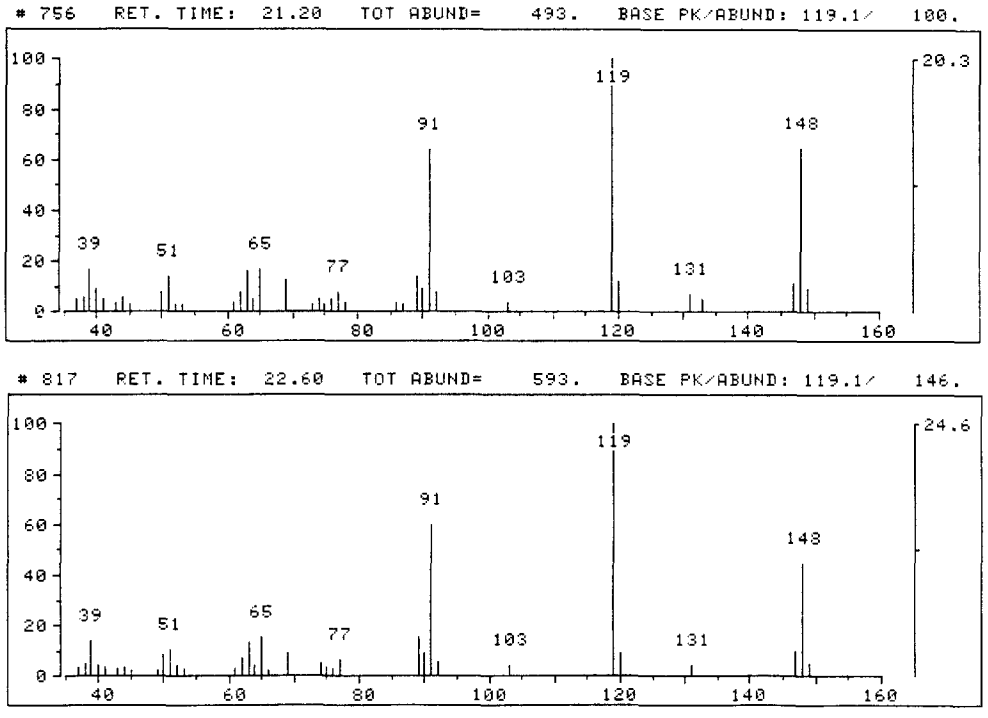

Fig. 3. EI mass spectra tentatively identified as representing 4- and 7-methyl-1(3*H*)-isobenzofuranone.

rial, the spectrum was thus interpreted as representing 2-acetylbenzaldehyde. This compound, which has been found as the principal ozonolysis product of 1-MN in aqueous solution [5], was synthesized according to published procedures [6]. However, comparison of its mass spectrum and relative gas chromatographic retention index (RRI) with the corresponding data of the unknown showed that the compounds were not identical.

Because of its isomeric composition and structural similarity with 2-acetylbenzaldehyde, and because the basic structure had also been identified as an ozonolysis product of 1-MN [5], 3-methyl-1(3*H*)-isobenzofuranone was synthesized as reference compound [7,8]. Matching mass spectra (upper and lower half of Fig. 2) and RRI prove its identity with the photo-oxidation product of 1-MN.

The mass spectra (Fig. 3) of two minor products (Nos. 4 and 5 in Fig. 1) closely resemble the published mass spectrum of 5-methyl-1(3*H*)-isobenzofuranone. They are thus interpreted as representing the isomeric compounds 4- and 7-methyl-1(3*H*)-isobenzofuranone.

The 1(3*H*)-isobenzofuranones have two fewer carbon atoms than 1-MN, which raises the question as to their mode of formation. The positions of the oxygen atoms in 3-methyl-1(3*H*)-isobenzofuranone correspond to the 1- and 4-positions in 1-MN. Therefore, we hypothesized that the initial step in its photo-decomposition was the formation, by reaction with singlet oxygen, of a 1,4-endoperoxide, as has been suggested for 2,4,6-trimethylphenol [8]. The endoperoxide could then decompose by homolytic cleavage of the O–O bond, rearrangement of the oxygen-centred radical site in the 4-position to the carbon-centred radical followed by ring closure to form the heterocyclic compound and expulsion of acetylene. Although initial tests had shown that adsorption by Carbosieve SIII, desorption with the Tekmar model 5010 Automatic Desorber and mass spectrometric analysis in selected ion monitoring mode was capable of detecting concentrations of acetylene in the upper nanomolar range, no trace of the gas was detected in sunlight-exposed seawater fortified with 1-MN.

It was thus deemed possible that instead of the hypothetical sequence outlined above the reaction might follow the scheme depicted in Fig. 4. 1-MN (**1**) should form the 2,3-dioxetane **2** as the first step in the reaction sequence, leading to the eventual formation of 3-methyl-1(3*H*)-isobenzofuranone (**7**). The two missing carbon atoms could then be eliminated as glyoxal (ethanedial, **4**) after homolytic cleavage of the O–O bond. The energetically unfavourable formation of the 1,4-diradical **3** may be avoided if ground state oxygen were to form a charge transfer complex with the 2,3-dioxetane **2**. Under the influence of sunlight this complex could then decompose in a concerted reaction without radical intermediates. The initial products of decomposition would be glyoxal **4** and a cyclic peroxide **5**. We suggest that rearrangement after homolytic cleavage of the peroxide bond and closure of the heterocyclic ring will lead to 3-hydroxy-1-methylisobenzofuran **6** as an intermediate. 1,4-Hydrogen shift and aromatization of the *ortho*-quinoid structure should then result in the final product **7**. In an analogous fashion, initial singlet oxygen addition to the unsubstituted benzene ring will lead to the 6,7-dioxetane. Its fragmentation yields the cyclic peroxide with a methyl-substituted quinoid benzene ring. After homolytic cleavage of the peroxide bond and

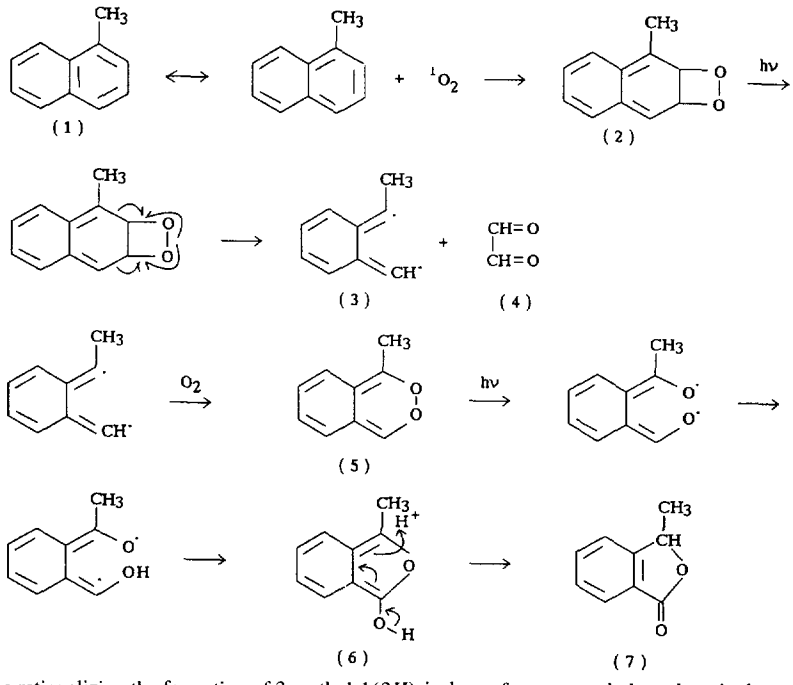

Fig. 4. Tentative reaction scheme rationalizing the formation of 3-methyl-1(3*H*)-isobenzofuranone and glyoxal as singlet oxygen induced photo-degradation products of 1-methylnaphthalene.

before closure of the heterocyclic ring, both of the oxygen-centred radical sites can rearrange to the energetically more favourable carbon-centred radicals with approximately equal probabilities. Depending upon which radical site rearranges first, the product is either 4- or 7-methyl-1(3*H*)-isobenzofuranone.

To test the hypothesis of glyoxal formation, the carbonyl compounds among the 1-MN photo-oxidation products were reacted with 2,4-dinitrophenylhydrazine. Comparison of retention times and coinjection with synthetic glyoxal 2,4-dinitrophenylosazone recrystallized from 1,4-dioxan (m.p. 322 °C, lit. 328 °C) showed that glyoxal indeed was a photo-oxidation product of 1-MN.

According to the tentative reaction sequence depicted in Fig. 4, 3-methyl-1(3*H*)-isobenzofuranone and glyoxal should form in approximately equal molar quantities. Using synthesized glyoxal 2,4-dinitrophenylosazone and 1-naphthaldehyde-2,4-dinitrophenylhydrazone as reference compounds to determine relative UV detector responses in HPLC analyses, and also using integrated TI chromatograms to compare the ion yields of 1-naphthaldehyde and 3-methyl-1(3*H*)-isobenzofuranone, we found that the amount of glyoxal formed was approximately one fifth the amount of 3-methyl-1(3*H*)-isobenzofuranone. The deficit of glyoxal may be due to non-quantitative reaction of 2,4-dinitrophenylhydrazine with the dialdehyde or to an instability greater than that of 3-methyl-1(3*H*)-isobenzofuranone under the experimental conditions.

The proposed reaction pathway is plausible for two reasons. The elimination of two carbon atoms from 1-MN can hardly be rationalized as non-simultaneous. Also, the recovery of glyoxal relative to 3-methyl-1(3*H*)-isobenzofuranone appears to be too high to suggest formation via secondary photo-decomposition of 1-MN photo-oxidation products.

The reaction sequence leading to the formation of 1-naphthaldehyde and 1-hydroxymethylnaphthalene must have started with abstraction of a hydrogen atom from the methyl group of 1-MN. Thus, there are strong indications that at least two different types of reaction with oxygen are involved in the photo-degradation of 1-MN:

1. reaction of ground state molecular oxygen with a benzyl radical formed by hydrogen abstraction from the methyl group;
2. addition of singlet molecular oxygen to the aromatic π-electron system.

Both types of reaction demand the participation of sensitizers. Hydrogen-abstracting triplet sensitizers have been found to occur in seawater [9]. Formation of singlet molecular oxygen is sensitized by components of marine humic material [10]. 1-MN has a weak absorption band within the spectral range of solar UV light at sea level; thus, formation of the identified products by reaction of excited triplet state 1-MN with triplet ground state oxygen cannot be excluded despite the low intersystem crossing quantum yield $\Phi_{ISC} = 0.48$ [11] and the low UV absorptivity of 1-MN (log $\epsilon = 2.4$ at 314 nm).

3.2. Rate of 1-MN photo-oxidation

For the experiment from 17 to 27 July 1995, the concentration of 1-MN was 2.61 mg l^{-1} in Baltic seawater (Salinity $= 11.171 \times 10^{-3}$). The saturation concentration was

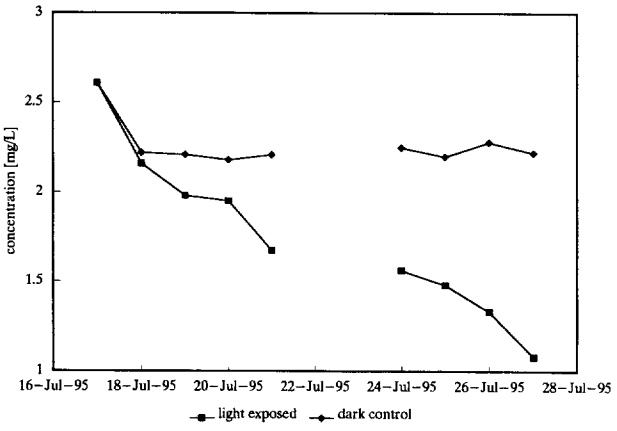

Fig. 5. Temporal development of 1-methylnaphthalene concentrations in sunlight-exposed seawater and in the corresponding dark control.

22.35 ± 0.70 mg l^{-1} at 25.8 °C. Microbial counts in daily samples were $24\,800 \pm 14\,350$ cells ml^{-1} in light-exposed water and $22\,980 \pm 15\,024$ cells ml^{-1} in the dark control. Thus, sterility was not attained, but the lack of positive temporal trends in the cell counts strongly suggests that the microorganisms were not feeding on and thus not degrading 1-MN. Intermittent increases in cell counts must have been due to additional microbial contamination during sampling and sample handling.

In Fig. 5 1-MN concentrations in the quartz vessel and in the amber glass vessel are plotted against time. Samples were collected daily around 0930 h except on 22–23 July, which was a weekend. The standard deviation of five analyses per sample was typically $\pm 4.4\%$ of the calculated concentration value regardless of whether the TIC or the MIC signal was integrated. During the first day of the experiment the concentration decreased from the T_0 value of 2.61 ± 0.05 mg l^{-1} to 2.16 ± 0.16 mg l^{-1} in the quartz and to 2.22 ± 0.12 mg l^{-1} in the amber glass vessel. Because the concentration of 1-MN in the dark control vessel then remained essentially constant until the end of the experiment, we assume that the initial decrease was caused by equilibration with the gas phase in the flasks and by wall adsorption effects. In the light-exposed water the concentration of 1-MN decreased further to a final value of 1.08 ± 0.06 mg l^{-1}. The daily light doses were not constant, so that the concentration decrease would not be expected to follow a simple function of time. Even if the photo-oxidation reaction was quasi first order with respect to 1-MN, it is not possible, therefore, rigorously to calculate the rate coefficient or the photo-oxidative halflife of 1-MN under the conditions of the experiment. Neither can quantum yields be determined, because the nature of the reacting system is not known with certainty. However, the concentration decrease of 1-MN from 2.16 ± 0.16 mg l^{-1} to the final concentration $C_{end} = 1.08 \pm 0.06$ mg l^{-1} in the light-exposed solution within 10 days might serve as a crude yardstick to evaluate the effectiveness of photo-oxidation reactions of 1-MN relative to biodegradation. The rate of photo-oxidation is expected to change depending upon the intensity of solar UV irradiation and the concentration of sensitizers in the water. The rate of microbial decomposition varies with temperature, nutrient availability and the structure of the microbial community [12–14]. The kinetics of microbial decomposition also are likely to differ from those of photo-oxidation; however, even allowing for these limits of comparability, the 50% decrease of the concentration of 1-MN after 10 days of exposure to sunlight is in the same order of magnitude as the 70% microbial metabolization of the aromatic fraction of a light Arabian crude oil after 20 days under optimal growth conditions [15].

Table 1
Compounds recovered after sunlight irradiation and their concentrations (μmol l^{-1})

1-Methylnaphthalene	3.36
3-Methyl-1(3*H*)-isobenzofuranone	0.20
Isomeric methyl-1(3*H*)-isobenzofuranone	0.02
Isomeric methyl-1(3*H*)-isobenzofuranone	0.02
1-Naphthaldehyde	0.06
1-Hydroxymethylnaphthalene	0.09
Glyoxal	0.04
Total concentration of identified photo-oxidation products	0.43

Table 1 shows that the combined identified photo-oxidation products in silica gel fractions 1–4 make up 12.8 mol% of the unreacted hydrocarbon. This percentage is barely increased by the small amount of an unidentified compound (peak 2 in Fig. 1). The decrease of 1-MN concentrations to 50% of the initial value thus implies that either primary and/or secondary decomposition products have escaped detection. Further research is needed to resolve this inconsistency.

4. Conclusions

Photo-oxidation and microbial decomposition of 1-MN appear to proceed at similar rates. The identification of 3-methyl-1(3*H*)-isobenzofuranone as photo-oxidation product of 1-MN in seawater and the mechanism rationalizing its formation may be used to infer the structures of photo-oxidation products of other alkyl-substituted naphthalenes. Thus, 2-methylnaphthalene should yield 1(3*H*)-isobenzofuranone (phthalide); depending upon the substitution pattern, di- and trimethylnaphthalenes should decompose to form isobenzofuranones carrying more than one methyl substituent. In the spring of 1992, one year after large quantities of crude oil were released during the Gulf conflict, compounds were isolated from coastal waters of the Persian Gulf the mass spectra of which strongly suggest such structures [2]. An example is given in Fig. 6; deviating from the original interpretation in [2], we suggest that the spectrum represents a 3,X-dimethyl-1(3*H*)-isobenzofuranone, where X denotes the unknown position of the second methyl group. This conjecture is supported by the intensity distribution of

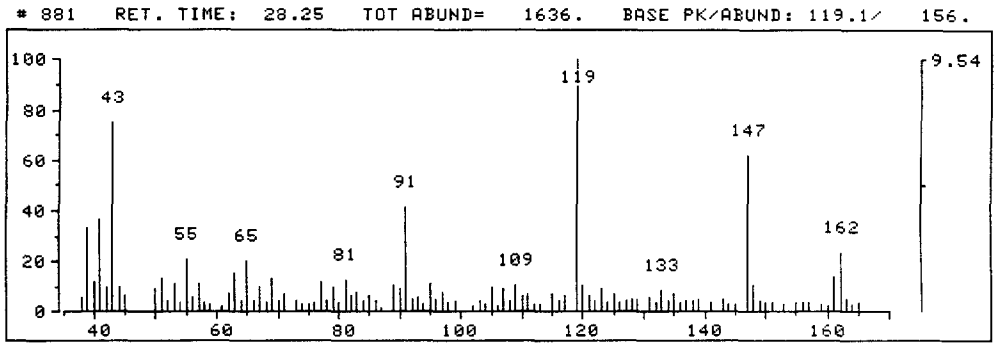

Fig. 6. EI mass spectrum of a compound isolated from Saudi Arabian Gulf coastal waters tentatively identified as 3,X-dimethyl-1(3*H*)isobenzofuranone, X denoting the unknown position of the second methyl group.

the principal fragments and the two gaps of 28 mass units which are also seen in the spectrum of 3-methyl-1(3*H*)-isobenzofuranone.

The detection of glyoxal as molecular fragment raises interesting questions: does photo-oxidation of 2-MN lead to methylglyoxal, does 2,3-dimethylnaphthalene form diacetyl? Do these α-dicarbonyl compounds form double Schiff bases and thus link amino components of the natural dissolved organic matter to result eventually in structures that could sensitize the formation of singlet oxygen? The effect would be autocatalysis. Do they interfere with microbial degradation because of their toxicity?

Acknowledgements

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