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The generation of singlet oxygen by petroleum and its fractions

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ABSTRACT

Quantum yields of singlet oxygen formation by diesel oil, samples of four different crude petroleum and some fractions of a Brazilian intermediate petroleum were measured at 315 nm, 355 nm, 400 nm and 450 nm both by pulsed LASER or Xe lamp, with analysis of singlet oxygen emission at 1270 nm. All samples generated singlet oxygen in dilute solution. Diesel oil has the highest quantum yield (0.49) and a Venezuelan crude the poorest (0.17). The aromatic, polar, asphaltene and maltene fractions of the Brazilian crude all generate singlet oxygen. Singlet oxygen formation was also observed when undiluted crude petroleum was analyzed.

1. Introduction

Petroleum is the main energy source in the modern world. Most of the oil is produced or transported in the ocean, and can cause severe damage to the environment. The recent disaster in the Gulf of Mexico, which released oil continuously for three months, reminded us of the fragility of our way of life. More than 4 million barrels of oil were spilled in the ocean water and almost 500 km of Louisiana's shoreline were affected. Almost one year after the accident a number of papers have been published [1–5] with respect to the effects of the spill on Louisiana's surroundings. This is not the first large scale oil spill on water, therefore it is essential to understand the chemistry of oil in the ocean environment in order to better deal with future problems.

Following an oil spill on water the petroleum may spread, sink, form water in oil emulsions or vice versa, evaporate, biodegrade and undergo sunlight induced photochemical transformations [6]. Once spilled, all these physical and chemical components act together to transform, degrade, and partially consume the oil.

As a highly complex matrix, petroleum can be fractionated into aliphatic, aromatic, resins, and asphaltenes. Recent studies in mass spectroscopy, electrospray ionization (ESI) and easy ambient sonic-spray ionization (EASI), have resulted in more detailed knowledge of the crude oil components [7,8]. Asphaltenes are the heaviest, most polyaromatic and least soluble portion of the petroleum [9–11] defined as the toluene soluble and normal alkane (by using small chains like pentane or heptane) non-soluble fraction. This is the most polar fraction of the crude oil presenting heteroatoms (N, O, and S) and metal ions [12–14] and with a C/H ratio close to 1.1, approximately 40% of the carbon atoms are present in polyaromatic structures with 4–10 rings. Further, the polyaromatic structures may be linked by aliphatic units or polar functional groups like —S—, —(CH_2)—, ethers and esters [15]. On the other hand, the normal alkane soluble fraction maltene shows a chemical composition similar to that of the petroleum itself and can be further fractioned by silica column chromatography into aliphatic, aromatic and polar groups.

Under solar irradiation singlet oxygen can be formed in the environment by naturally colored material [16,17] such as humic and fulvic acids. Further, the singlet oxygen thus formed plays a role in the oxidation of organic material and is involved in the enhancement of environmental phototoxicity [18].

Crude petroleum strongly absorbs UV and visible solar radiation and photochemical processes are known to be important to overall environmental weathering [6,19,20]. However, the mechanism of photochemical petroleum weathering has been little studied and the role of singlet oxygen in this process is unknown [21].

What information exists is mostly indirect. The photo oxidation of fuel oil was inhibited by beta-carotene, a good singlet oxygen quencher, and the authors concluded that the reaction involved singlet oxygen [22]. Further, the photo oxidation of dimethylnaphthalenes sensitized by petroleum was found to involve singlet oxygen [23]. On the other hand, beta-carotene or other singlet oxygen quenchers did not affect the photo oxidation of a crude oil and it was concluded that in this case singlet oxygen was not involved [24].

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Dilute maltene fractions of petroleum have also been irradiated and the quantity of singlet oxygen was determined by measuring the consumption of a known chemical singlet oxygen quencher, tetramethylethylene. The quantum yields measured using this indirect method were found to be wavelength dependent [25]. Short wavelength UV light gave higher yields. Undiluted maltene gave a much lower yield.

If singlet oxygen is to have a role in petroleum weathering, it must be formed. In this study the quantum yield of singlet oxygen was measured for various types of crude petroleum using a direct method: analysis of singlet oxygen phosphorescence emission at 1270 nm with a flash photolysis apparatus. All samples were found to be singlet oxygen generators in dilute solutions both in the UV region (355 nm) as well as the visible (400–532 nm), and to be mainly due to the aromatic fraction. The singlet oxygen signal at 1270 nm was also observed in undiluted petroleum.

2. Materials and methods

Singlet oxygen was generated by excitation of petroleum and its fractions or a standard using the doubled 532 nm or tripled 355 nm emission from a 5 ns Nd:YAG Continuum laser or by a Xe flashlamp both coupled to an Edinburgh Analytical Instruments LS 920 time resolved flourimeter. For the 315 nm, 400 nm and 450 nm excitations, samples were pumped by a Xe flash lamp from Oriel Instruments. The singlet oxygen emission at 1270 nm was detected using a peltier cooled NIR-PMT Module H10330-45 from Hamamatsu. The laser power was measured with a COHERENT radiometer model FM.

Quantum yields were obtained by measuring the 1270 nm time dependent emission intensity of absorbance matched sample and standard (absorbance 0.30). The laser pulse energy was varied and the signal intensity was extrapolated back to time zero. Signal intensity was plotted against laser energy for both sample and standard. The ratio of the slopes of the sample relative to that of the standard at low laser energies, gives the ratio of the quantum yields. The standard used at 355 nm was phenalenone. Tetraphenylporphyrin was used at 532 nm.

Quantum yields for anthracene consumption by singlet oxygen were determined using a 1.7×10^{-5} M solution of tetraphenylporphyrin in chlorobenzene to absorb the 632.8 nm emission from an Oriel He/Ne laser. The rate of singlet oxygen generation was measured substituting 1,3-diphenylisobenzofuran (DPBF) for anthracene. The concentration of DPBF was varied from 1.25 to 6.25×10^{-6} M and the consumption of DPBF was followed by fluorescence using a F-4500 Hitachi Spectrofluorimeter. The rate of consumption of DPBF extrapolated to infinite concentration was used as the rate of singlet oxygen formation. Anthracene consumption was also followed by fluorescence.

Petroleum samples were obtained from CENPES (Centro de Pesquisas da Petrobras) and the fractions used were separated from an intermediate Brazilian petroleum previously studied [26] using standard procedures (ASTM D2007). Petroleum fractionation was performed following literature procedures [27].

Singlet oxygen quenching rate constants for maltene, aromatics, polar and asphaltene fractions from the Brazilian petroleum were obtained by quenching the singlet oxygen generated from phenalenone in chlorobenzene.

3. Results and discussion

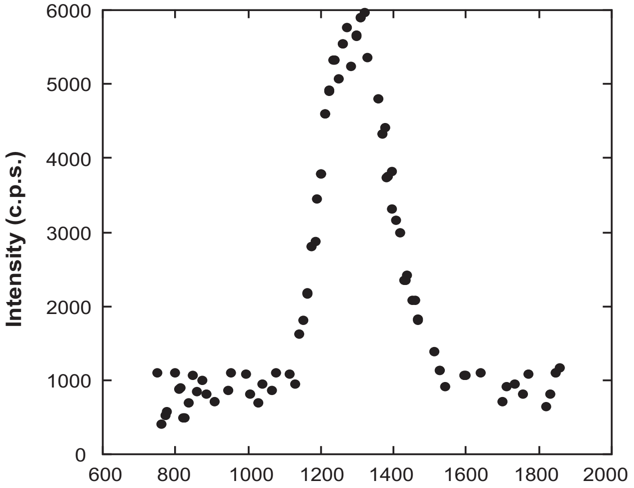

Fig. 1. Emission spectra of singlet oxygen in petroleum.

In this study the quantum yield of singlet oxygen was measured by following the initial intensity of emission at 1270 nm. This emission is widely regarded as proof of singlet oxygen formation [28], however, in this case it is possible that low energy triplets of petroleum components could be emitting in the same spectral region. It was therefore verified that the observed emission was in fact due to singlet oxygen. The emission spectra (Fig. 1) show the emission maximum and bandwidth expected for singlet oxygen. This signal decays with first order kinetics (Fig. 2) and has a lifetime (34 μs) as expected for singlet oxygen in acetonitrile [29]. Further the signal is eliminated when the solvent is nitrogen purged.

Quantum yields were obtained by measuring the emission intensity shortly after the Nd:YAG laser pulse (the first 5 μs) and extrapolating the intensity back to time zero. The energy of the laser pulse was then varied and the signal at low pulse energies was plotted against the laser pulse energy. It was found that at higher pulse energies the sample tended to saturate and the signal approximated to a plateau (Fig. 2). So the initial linear portion of the curve was used in all cases. This was compared with the signal generated, in the same way, by a sample of phenalenone in chlorobenzene with the same absorption at 355 nm. The ratio of the slopes (Fig. 3) gave the ratio of the quantum yields [29,30].

Phenalenone has been used as a standard for singlet oxygen generation in a number of solvents [31], giving a quantum yield close or equal to one in all solvents measured, however its quantum yield of singlet oxygen formation in chlorobenzene was not found in the literature. Therefore the quantum yield for singlet oxygen formation by phenalenone in chlorobenzene was measured and found to be 0.97 ± 0.06, by comparing with its yield in benzene and toluene

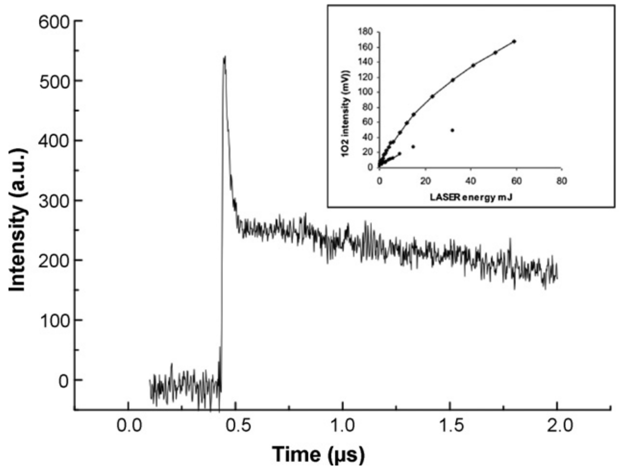

Fig. 2. Singlet oxygen decay in toluene. In the box singlet oxygen signal at time = 0 versus LASER energy: phenalenone (upper trace) and petroleum (lower trace).

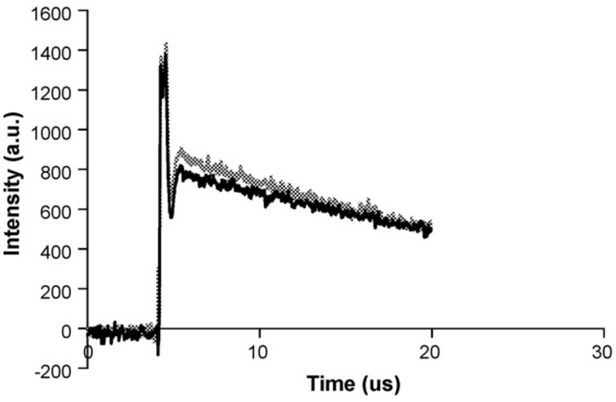

Fig. 3. Singlet oxygen decay in toluene (black) and CCl_4 (gray).

which had previously been measured [30]. A comparison of the initial signal intensity of absorbance matched samples gave the values shown in Table 1. The signal was corrected for differences in refractive index [32] using the standard procedure used for fluorescence corrections (n_u^2/n_s^2) and the value obtained is essentially the same as that in toluene or benzene.

Using this methodology, the quantum yield of singlet oxygen formation by diesel oil, four different crude petroleum and petroleum fractions diluted in chlorobenzene were measured and the results are given in Tables 1 and 2. There is a rough inverse correlation between the viscosity and the singlet oxygen quantum yield, the lightest crude gave the highest yields. Diesel oil, which has a much lower viscosity, is an even better singlet oxygen generator. It is worthwhile to note that viscosity increases with the relative concentration of the higher molecular weight components in the oil. If these absorb strongly at 355 nm and are poor generators of singlet oxygen relative to the lighter weight components (which absorb at 355 nm), the present results can be explained. However, there is also a very good correlation between the viscosity and the asphaltene concentration of the oils used in this study. An alternative explanation involves the concentration of the asphaltenes in these oils. The asphaltene fraction is the heaviest and the strongest absorbing fraction at 355 nm. As shown below, it is also the fraction which least generates singlet oxygen. Those oils containing more asphaltene would have a greater fraction of the light absorbed by this fraction and would, consequently generate less singlet oxygen.

Table 1
Singlet oxygen quantum yield for diesel oil and different crude petroleum in chlorobenzene and excitation at 355 nm.

Sample	Φ $^1O_2$*
Diesel oil	0.49 ± (0.04)
Mexican petroleum	0.35 ± (0.03)
Arabian petroleum	0.30 ± (0.05)
Brazilian petroleum	0.20 ± (0.04)
Venezuelane petroleum	0.17 ± (0.04)

Table 2
Singlet oxygen quantum yield for fractions of Brazilian petroleum.

Sample	Φ $^1O_2$ at different excitation wavelengths (nm)			
	315	355[a]	400	450
Maltene	0.25	0.28	0.19	0.27
Aromatics	0.15	0.40	0.42	0.42
Polar	0.53	0.24	0.31	0.51
Asphaltene	0.11	0.15	0.18	0.21
Brazilian petroleum	0.23	0.20	0.30	0.32

[a] Absorption coefficients at 355 nm computed in terms of mass: maltene (2.16), aromatics (0.33), polar (6.85) and asphaltene (16.03).

Table 3
Stern–Volmer quenching rates for singlet oxygen.

Sample	k (g L^{-1} s^{-1})
Maltene	2.60×10^6
Aromatics	1.71×10^6
Polar	1.86×10^6
Asphaltene	6.72×10^6
Brazilian petroleum	5.08×10^6

In order to further understand the fate of singlet oxygen in the presence of petroleum, the rate constants for singlet oxygen quenching (k_q) by the Brazilian crude petroleum and its fractions were measured. As can be seen in Table 3 and Fig. 4, the asphaltene fraction shows a quenching rate two to three times greater than for the other fractions and its k_q is almost 40% larger than the value for the respective crude oil. The third most efficient quencher is the maltene fraction followed by the polar and aromatic fractions. As to why the asphaltene fraction is the best singlet oxygen quencher can be rationalized if one considers the chemical composition of this fraction. As mentioned before [12–14] the asphaltene is the more polar fraction from the crude oil, containing N, S and metallic cations such as Ni and V [15]. Also, the asphaltenes are the heaviest fraction of the crude oil. These combined characteristics can be responsible for the larger values of k_q reported in Table 3. Further, it is worthwhile noting that the second best quencher studied here is the crude oil, in which the asphaltene is solubilized. These results point to the asphaltenes as being the more photochemically important fraction in spilled petroleum, as this is the fraction that absorbs most light, least generates singlet oxygen, and is the best singlet oxygen quencher among the petroleum fractions.

Analysis of the Brazilian crude oil in toluene, using the second harmonic of the Nd:YAG at 532 nm and tetraphenylporphyrin as standard (Φ = 0.80) [31], gave a quantum yield of singlet oxygen of 0.11 ± 0.02, compared with 0.20 ± 0.02 at 355 nm.

A direct comparison of these results with those obtained by Lichtenthaler et al. [25] is not possible since the oil samples were not the same. However, all the quantum yields found by this direct method (including diesel oil) are lower than the quantum yield of about 0.6 found, indirectly, when a light maltene fraction of crude oil in toluene as irradiated at 366 nm. In that study tetramethylethylene was used as a trap for singlet oxygen and it is possible that free radical reactions and loss of some substrate by evaporation may have been attributed to reaction with singlet oxygen. These authors found that the use of visible irradiation in the range of 400–500 nm gave values four times lower, and above 550 nm the quantum yield decreased even further. In the case of the Brazilian crude, Table 2 shows that the quantum yield is less sensitive to wavelength. No significant change was seen when going from 355 to 532 nm. There

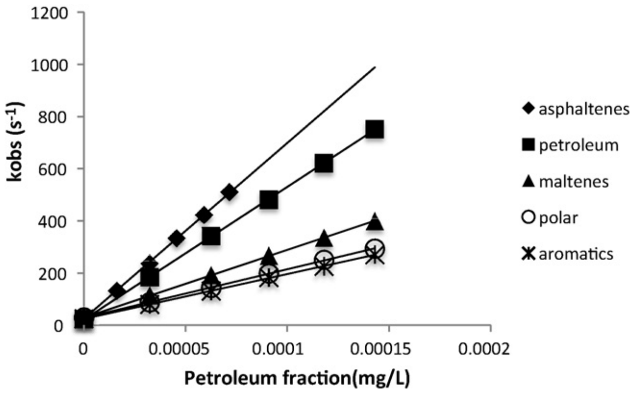

Fig. 4. Stern–Volmer plot for the singlet oxygen quenching by petroleum and its fractions.

is probably no strict relationship between singlet oxygen quantum yield and wavelength due to the multitude of possible absorbing structures at each wavelength.

Petroleum is often classified according to general composition and separated into aliphatic, aromatic, polar and asphaltene fractions. While it is impossible to determine what specific molecular components are responsible for singlet oxygen generation, it is possible to analyze these general fractions. Therefore, in order to obtain more information on the source of the singlet oxygen, a Brazilian petroleum (Bacia de Campos, in the state of Rio de Janeiro), which has been well characterized [27,32,33] was separated into asphaltene and maltene fractions and the maltene was further fractionated into aliphatic, aromatic and polar fractions [26]. As expected, the aliphatic fraction did not absorb at the studied wavelengths and was not further evaluated. The other fractions were used to generate singlet oxygen, in toluene, using the same methodology and the quantum yields are presented in Table 2. The aromatic and the polar fraction are the strongest generators of singlet oxygen while the asphaltene fraction gives the lowest quantum yield. It was found that the asphaltene fraction of this intermediate petroleum was about half as efficient in generating singlet oxygen as was the maltene fraction. Lichtenthaler et al. had previously found that, in their case, the asphaltene fraction was about three times less efficient than the lighter maltene fraction. These results are in reasonable agreement.

It might be expected that the quantum yield for singlet oxygen in the Brazilian petroleum would be the sum of the quantum yields for the individual fractions times the fraction of light absorbed by each fraction as expressed in the equation below:

$$\phi_{D(\text{petroleum})} = (\phi_D \times f)_{\text{maltene}} + (\phi_D \times f)_{\text{asphaltene}}$$

This was tested using the data from Table 2, where *f* is the fraction of light absorbed by each component. The calculated value using this equation was found to be 0.22, which is in good agreement with the experimental value of 0.20 for the unfractionated crude petroleum.

An undiluted sample of Brazilian petroleum was tested for singlet oxygen generation using front face excitation. A weak signal was observed at 1270 nm with a lifetime of about 500 ns. However, due to the extremely high absorbance, it was not possible to determine the quantum yield of singlet oxygen generation with this methodology.

It is known that polycyclic aromatic hydrocarbons such as those found in petroleum are photo-chemically degraded in the environment [34–37]. Mechanisms involving singlet oxygen could explain this degradation but mechanistic studies are lacking. The quantum yield of consumption of anthracene in water upon direct irradiation at 360 nm has been found to be 0.003 [38]. Although anthracene is a good singlet oxygen generator [31] and quenches singlet oxygen with a rate constant of 3.5×10^5 L m^{-1} s^{-1} in CCl$_4$ [39], it is not known how much of this quenching is chemical and how much is physical.

We therefore measured the quantum yield of chemical quenching (leading to consumption of anthracene) by irradiating tetraphenylporphyrin at 632 nm using a He/Ne laser to generate singlet oxygen. The quantity of singlet oxygen generated was measured in the same system by measuring the consumption of 1,3-diphenylisobenzofuran. Using a one millimolar solution in chlorobenzene a quantum yield of 0.0015 was found. Using the known rate constant for singlet oxygen decay in chlorobenzene ($\text{kd} = 2.2 \times 10^4\ \text{s}^{-1}$) [39] and the known rate of the sum of physical and chemical quenching ($\text{kc} + \text{kp} = 3.5 \times 10^5$) and the equation:

$$\frac{1}{\Phi} = 1 + \frac{\text{kp}}{\text{kc}} + \frac{\text{kd}}{\text{kc}}[\text{An}]$$

A value for kc of 3.3×10^4 L M^{-1} s^{-1} was estimated.

The lifetime of singlet oxygen is ten times shorter in water and the solubility of anthracene is very low (4×10^{-7} M) [40]. If the rate constant for chemical quenching of singlet oxygen by anthracene in water is similar to that in chlorobenzene, the measured quantum yield of anthracene consumption in water [38] is five orders of magnitude higher than it would be expected for a mechanism involving singlet oxygen. In the oil phase, however, singlet oxygen may well be degrading PAHs such as anthracene.

4. Conclusion

We have found that petroleum is able to generate singlet oxygen in dilute solution with quantum yields inversely related to the asphaltene concentration. The lightest crudes give the highest yields while diesel oil (0.49) is an even better generator. The aromatic and polar fractions are the best singlet oxygen generators while asphaltene the least, at wavelengths from 315 to 532 nm. Since asphaltene strongly absorbs sunlight, it reduces the quantum yield for singlet oxygen formation when present. Visible light is also capable of generating singlet oxygen with moderate quantum yields. When photochemical petroleum weathering is considered, the quantity of singlet oxygen generated will depend on the type and composition of petroleum involved, but in the presence of sunlight it is probably generated in an appreciable quantity. This study shows that singlet oxygen formation is a general process upon solar irradiation of petroleum and its derivatives and further that singlet oxygen should be considered as a reactive species that can possibly be related to the degradation of PAHs in oil spills.

Acknowledgments

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