Visible light-induced desulfurization technique for light oil

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A visible light-induced desulfurization process for light oil, effected by electron-transfer photooxygenation and liquid–liquid extraction, allows the deep desulfurization of light oil under moderate conditions and without hydrogen.

The desulfurization of light oil has become one of the urgent problems of the world.[1] In order to protect against environmental contamination, the sulfur level in diesel fuels is presently limited to 0.05 wt% in Japan and Europe, and this will certainly be tightened in the near future. The current technology of hydrodesulfurization (HDS), when adopted on an industrial scale, can desulfurize aliphatic and acyclic sulfur-containing compounds adequately. The above process, however, when treating dibenzothiophene and its derivatives (DBTs),[2–4] apparently fails to reach the new specifications imposed by recent Clean Air Regulations. Thus, to produce light oil containing a very low level sulfur requires inevitably rather severe conditions. For the development of an energy-saving desulfurization process, a new approach is needed which isn't limited to the conventional HDS method.

As reported by Berthou and Vignier,[5] DBTs in spilled crude oil are sunlight-photooxidized to DBT sulfoxide (DBT-O) and DBT sulfone (DBT-O_2) in sea water. These sulfur-oxygenated DBTs are highly polarized and are water-soluble. The application of this photochemical oxidation to desulfurization has been realized in our previous studies, using oil–water[6,7] and oil–polar solvent[8] two-phase systems, and in which the desulfurization of light oil to a sulfur content of less than 0.05 wt% has been achieved successfully. However, UV irradiation was found to be essential to oxidize DBTs and desulfurization hardly progressed at wavelength of $\lambda > 400$ nm.

Electron-transfer type photosensitizers, such as cyano-substituted anthracene, differ from the usual energy-transfer type photosensitizers, and act as the anode by absorbing the wavelength of light equivalent to their lowest excitation energy. The sulfur-containing compounds, having the free electron on the S atom, are thought to be readily one-electron oxidized by this type of photosensitizer. In this work, we consider such a photoprocess applied to the indirect photooxygenation of DBTs and thus to the desulfurization of DBTs in light oil.

A schematic electron-transfer process between 9,10-dicyanoanthracene (DCA) and DBT in MeCN is shown in Fig. 1. DCA has a relatively low reduction potential and can be excited at wavelengths greater than 400 nm. DCA exhibits a strong, blue fluorescence in both polar and non-polar solvents. This blue fluorescence is quenched by adding DBT with the rate constant of $k_{\mathrm{q,\,DBT}} = 1.75 \times 10^{10}$ L mol^{-1} s^{-1}, and a yellow fluorescence is then exhibited. Exciplex emission is observed only in non-polar solvents, and not in MeCN and MeOH; this suggests that dissociation of the ion pairs occurs only in the most polar solvents.

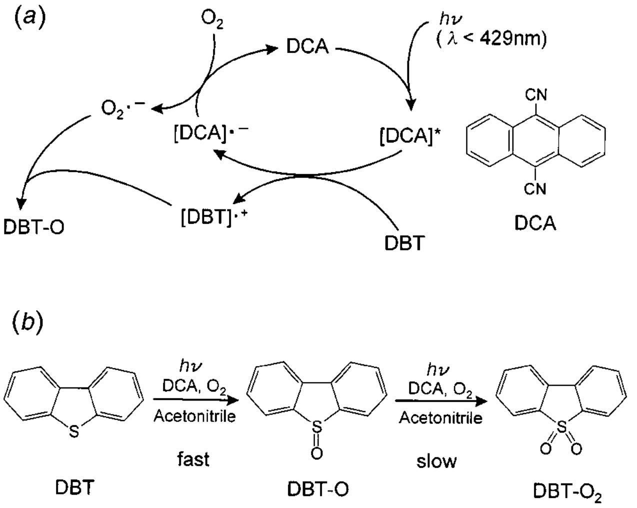

Fig. 1 (*a*) Electron-transfer process occurring in MeCN between DCA, DBT and oxygen. (*b*) Schematic representation of the reaction route of DBT by DCA sensitized photooxygenation.

An MeCN solution containing DBT and DCA was irradiated to visible light of wavelength $\lambda > 400$ nm (main emission peak: 406 nm), generated by a high-pressure mercury lamp with a 3 wt% $NaNO_2$ solution filter.[9] As shown in Fig. 2, only in MeCN were the corresponding sulfoxide (DBT-O) and sulfone (DBT-O_2) photogenerated at high yield, whereas no reaction was observed in protic solvents such as MeOH and Pr^{i}OH or in non-polar solvents. This behavior is expected for a process proceeding *via* an intermediate ion pair, since such a pair will be too poorly solvated in non-polar solvents to be separated. Other photosensitizers such as *p*-benzoquinone or 1-cyanonaphthalene are not applicable to this process, since the oxidation potential of the former is lower than the reduction potential for O_2 and the latter is excited at wavelength shorter than 320 nm. These findings suggest that DCA is the most suitable photosensitizer for the photooxygenation of DBT, which seems to proceed *via* the three steps shown schematically in Fig. 1. These are (i) photoexcitation of DCA, (ii) one-electron oxidation of DBT and one-electron reduction of O_2 (generation of superoxide ion $O_2^{\cdot -}$) and (iii) combination of radical ion pairs (DBT$^{\cdot +}$

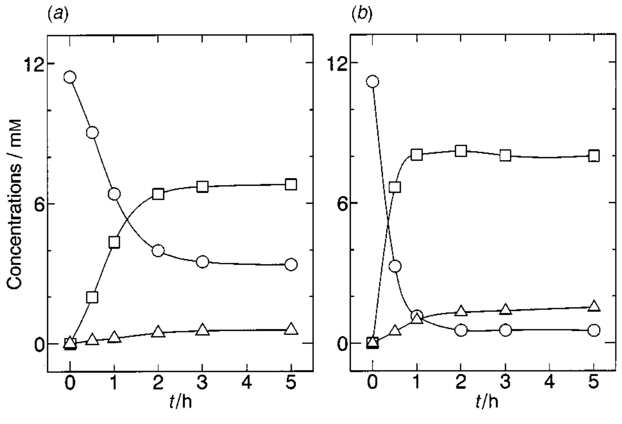

Fig. 2 Time-course variation for the concentrations of (○) DBT, (□) DBT-O and (△) DBT-O_2 by DCA photosensitized reaction in MeCN. The initial concentrations of DCA are (*a*) 0.02 and (*b*) 0.1 mM.

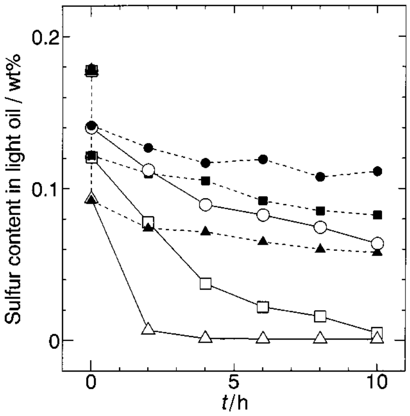

Fig. 3 Time-course variation of sulfur content in light oil for differing solution volume ratios: MeCN:light oil = (○,●) 1:1, (□,■) 3:1 and (△,▲) 7:1; filled symbols = without DCA, open symbols = with DCA.

and $O_2^{\cdot -}$). In alcoholic solvents, the oxygenation seems to be prevented, owing to the shorter lifetime for $O_2^{\cdot -}$. Bacciochi *et al.*[10] have suggested the C–S cleavage mechanism for the electron-transfer reaction of benzyl phenyl sulfide, but DBT gave only the S oxidation product, as mentioned in the case of diphenyl sulfide.[11] This is attributable to a stabilization of the C–S bond of DBT by thiophenic heterocycles. The rate of DBT oxidation decreased with photoirradiation time, as shown in Fig. 2(*a*), since the DBT-O formed also quenches the DCA fluorescence ($k_{\mathrm{q,\,DBT\text{-}O}}$ = 7.37 × 10^9 L mol^{-1} s^{-1}) and competitive electron-transfer occurs. This problem can be solved by adding a larger quantity of DCA [Fig. 2(*b*)]. The two photoproducts of DBT, DBT-O and DBT-O_2, are both highly polarized and insoluble in non-polar light oil.[12] Thus the process has potential for the desulfurization of light oil.

The above photoprocess was applied to the desulfurization of light oil containing ca. 0.18 wt% sulfur, which is below the previous regulation in Japan (0.2 wt%). Light oil (50–200 ml) and MeCN (200–350 ml) saturated with DCA were introduced into the reaction vessel at MeCN:light oil volume ratios of 1:1, 3:1 or 7:1 v/v. The solutions were photoirradiated using a high-pressure mercury lamp with a 3 wt% $NaNO_2$ solution filter, combined with air bubbling at atmospheric pressure.

Certain quantities of DBTs from the light oil in the light oil–MeCN two-phase system transfer into the MeCN phase, together with other aromatics. The photoirradiation of the two-phase system thus causes the oxidation of the DBTs in the MeCN, resulting in the successive removal of the DBTs from the light oil phase.[8] Fig. 3 shows the effect of the addition of DCA on the time-course variation of the sulfur content in the light oil, with respect also to variations in the MeCN:light oil volume ratio. The data points, at an irradiation time of zero, show the distribution equilibria for the sulfur contents in the two-phase systems. Without DCA, the sulfur content was reduced only slightly, since the light oil contains three-ring aromatics which absorb visible light only weakly. The reduction rate for the sulfur content was enhanced drastically however by the addition of DCA. For an MeCN:light oil volume ratio of 3:1, 2 h of irradiation decreased the sulfur level to 0.05 wt%, and 10 h of irradiation decreased the value to 0.005 wt%, which is the value presently strictly legislated in Sweden. Light oil containing such a low sulfur level has not been achieved so far by the HDS method, even under severe operating conditions at 673 K.[3] Thus, the present method is applicable as an energy-saving deep desulfurization process to meet with the newest regulation for sulfur content in light oil, and requires only air bubbling and irradiation with visible light, avoiding the use of hydrogen and high pressure.

The present study thus describes a novel desulfurization process for light oil, effected by the combination of electron-transfer photooxygenation and liquid–liquid extraction using an oil–MeCN two-phase system. This could be developed as a desulfurization process utilizing solar irradiation as a light source. Work is in progress to develop the overall process, including a method for subsequent recovery of DCA from the resulting solutions.

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