Photodegradation of Surfactants. VII.

Peroxide and Aldehyde Formation in the Photocatalyzed Oxidation of Nonionic Surfactants

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The non-ionic surfactant p-nonylphenyl poly(oxyethylene) ether undergoes photodegradation in irradiated heterogeneous TiO₂ dispersion. The intermediacy of peroxides, aldehydes, and carboxylic acids is observed in the photodegradation of the surfactant to CO₂. Amounts of the formed intermediate compounds are influenced by pH of the reaction mixture.

1 Introduction

The photodegradation of surfactants can be classified into three steps: (1) primary degradation (cation radical formation, peroxide formation and hydroxylation, etc.); (2) secondary degradation (aromatic ring opening, carboxylic acid formation, etc.); and (3) ultimate degradation (mineralization to CO₂).

The heterogeneous photocatalytic pathway is very complex owing to the formation of several intermediate species which retard CO₂ evolution, but none of which have hitherto been identified or described in detail. We have recently reported extensively on the photodegradation of a large number of surfactants (anionic, cationic, and nonionic) catalyzed by TiO₂ semiconductor particles1)–7).

This paper deals with the intermediacy mainly of peroxides and aldehydes in the photodegradation of nonionic surfactants and of model compounds which make up the surfactant structure. As well, we examine the pH dependence of intermediate formation.

2 Experimental

The p-nonylphenyl poly(oxyethylene) ethers \( [C_{n}H_{19-C_{n}}H_{4-}O-(CH_{2}CH_{2}O)_{n}-H \) (NPE-n), where \( n=7, 9, 17, 50 \) were used as supplied by Miyoshi Oil & Fat Co. Ltd. A heterogeneous suspension containing surfactant solution (50 mL) and anatase TiO₂ (0.1 g, Degussa P-25, surface area 55 m²/g) was contained in a 70 mL-glass vessel and was magnetically stirred during illumination with a Hg-lamp (>330 nm). After an appropriate irradiation time, the suspended solution was sampled, centrifuged and subsequently filtered (pore size 0.22 µm). The phenoxy moieties were monitored by UV absorption (222 nm). Formation of peroxides was assayed iodometrically with potassium iodide (detection 356 nm)8). The quantity of aldehydes in the degraded solution was determined by Nash’s procedure: the aldehyde reacts with acetylacetone, acetic acid, and ammonium acetate and the absorbance of the resulting diacetyldihydrolutidine is monitored at 412 nm9). The temporal evolution of carboxylic acids formed was followed at 570 nm by treating the sample with magnesium ribbon and chromotropic acid in a sulfuric acid solution10). Evolved CO₂ was analyzed by TCD gas chromatography as described previously11).

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3 Results and Discussion

Fig.-1 summarizes the temporal changes in the phenoxy absorption, the formation of peroxide and aldehyde species, and CO₂ evolution at various pH's in the photodegradation of NPE-50. At neutral pH (ca. 5–6), the phenoxy moiety was rapidly cleaved within ca. 1.5 h of irradiation. By contrast, the degradation was slow in alkaline media. Curiously, the absorption peak of the phenoxy moiety increased after 2 h, probably an oxidized intermediate that could result in increase in UV absorption formed. The peroxide formed faster than either the aldehyde, the carboxylic acid, or the CO₂. The concentration of peroxides reached a maximum value after 0.5–1 h of irradiation, and then they decomposed gradually. The formation of peroxide followed the order: alkaline (pH=12) < neutral (pH =5–6) < acidic (pH=2). Possibly, the peroxides formed are not stable in alkaline media and easily undergo decomposition, resulting in the peroxide diminution. In acidic media, the peroxides are more stable. The aldehyde, carboxylic acid, and CO₂ formed concomitantly with peroxide and increased gradually with irradiation time. It should be noted that the analytical method used for aldehydes addresses mainly formaldehyde, but small quantities of acetaldehyde can also be detected. The amount of aldehyde produced in alkaline solution was greater than that in neutral or in acidic media. In addition, more aldehyde formed than peroxide. Further photooxidation of aldehyde was ascertained by the formation of formic acid and/or acetic acid. The quantity of these acids decreased in the order: pH=12 > pH =5–6 > pH=2. Finally, a greater quantity of CO₂ evolved under neutral conditions than in alkaline or in acidic media. Note that the CO₂ evolved in alkaline solution was measured by adding 0.5 mL of concentrated HCl to the solution after some appropriate irradiation time. The mineralization yield was ca. 15 % after 8 h of irradiation at pH=5–6.

The effect of the number of ethoxyl group number in NPE-ₙ on the peroxide formation was also examined. The results show that the concentration of peroxides formed in the photodegradation process increased with the number of ethoxyl groups, n : NPE-7 < NPE-9 < NPE-17 < NPE-50. As noted earlier¹⁻⁶, the aromatic and the ethoxyl fragments in the NPE ethers undergo competitive adsorption and degradation. Consequently, owing to the higher number of ethoxyl groups in NPE-50, the peroxide degradation appears to be retarded.

The experimental data also show that for the TiO₂-free surfactant system, no peroxide was formed after more than 10 h of irradiation, and that under dark conditions, little if any peroxide (<1×10⁻⁴ M) formed in less than 7 h for the

* (reported as M).

Fig.-1 Photodegradation of NPE-50 (0.1 mM, 50 mL) in air-equilibrated aqueous suspensions of TiO₂ (100 mg) under Hg-lamp illumination (>330 nm) at □ pH=2, ○ pH=5–6, and pH=12.
surfactant solution containing TiO₂ particles. Clearly, both TiO₂ and UV light are essential factors for the formation of peroxides. Moreover, after 7 h of irradiation of a surfactant-free TiO₂ suspension, the amount of peroxide formed was less than 1 × 10⁻⁵ M. This fact implies that peroxides resulted mainly from the surfactant, and not from water.

Some model compounds (used as reference) were also photodegraded to examine some of the details of competitive adsorption and photooxidation of the alkyl chain, the phenoxy group, and the long ethoxyl chain in NPE structure. The formation of peroxide and aldehyde from phenol (PhOH), 2-phenoxyethanol (PhOCH₂CH₂OH), ethylene glycol (EG), and polyethylene glycol-1000 (PEG) are illustrated in Fig.-2. Under otherwise identical conditions, the quantities of peroxide formed from PhOH and PhOCH₂CH₂OH were greater than those from EG and PEG. The peroxides originate predominantly from the phenoxy moiety. By contrast, aldehyde originates principally from ethoxylated substrates; thus, the phenoxy species such as PhOH and PhOCH₂CH₂OH produced less aldehydes than EG and PEG. Consequently, less formic acid formed from the photooxidation of phenoxy species. Both aldehyde and formic acid formed readily from the ethoxy groups. To the extent that the temporal course of formation and quantity of aldehydes and formic acids produced within 6 h of irradiation exhibited similar trends for both EG and PEG, we infer that the ethoxyl chain in NPE (and thus on NPE-ₙ ethers) is not cleaved randomly but sequentially one by one from the terminal ethoxyl group. Although phenol and 2-phenoxyethanol were readily oxidized to peroxides, the latter necessitated longer periods to decompose to give the aldehyde and formic acid. The peroxides formed from ethoxyl groups easily degraded to aldehyde within a shorter time; only the trace of peroxide could be detected.

We conclude that the phenoxy moiety in the non-ionic NPE structure was predominantly photooxidized to give peroxides, particularly in acidic side, and that the ethoxyl chain in NPE was more quickly photodegraded to aldehyde, especially in alkaline solution.

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References

界面活性剤の光分解（第7報）
非イオン界面活性剤の光触媒酸化における
過酸化物とアルデヒド生成

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p-ノニルフェニル＝ポリ (オキシエチレン)＝エーテルの非イオン系界面活性剤を不均一系 TiO₂分散系にお
いて光分解を行った。CO₂の完全無機化反応に至る過
酸化物、アルデヒド及びカルボン酸形成中間生成物を光
酸化反応における pH 依存性と共に検討した。