

Heterogeneous photocatalytic oxidation of naphthalenes on zirconium and germanium phosphates

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Abstract

Irradiated zirconium and germanium phosphates are used as photocatalysts for the oxidation of electron-rich molecules of naphthalenes in air-saturated acetonitrile. Some of these reactions are selective: phthalic anhydride is the main reaction product (yield 70%) in the photo-oxidation of naphthalene. A mechanism involving the formation of radical cations via the interaction of naphthalene with irradiated zirconium phosphate and a likely scheme of reaction are proposed.

Keywords: Photocatalytic oxidation; Naphthalenes; Zirconium phosphates; Germanium phosphates

1. Introduction

In the field of heterogeneous photo-oxidation we are interested in the photocatalytic activity of the phosphates of tetravalent elements (Zr, Ti, Ge, Sn) for the oxidation of aromatic substrates. Our previous work showed the catalytic activity of Zr phosphates in the photo-oxidation of alkylbenzenes under mild conditions [1]. In all the reactions only side-chain oxygenation was observed. Moreover, the importance of the role of the different acidic sites (Brønsted and Lewis) present on the surface of these materials was evidenced.

The present investigation concerns the photo-oxidation of naphthalenes at 20–22 °C in the presence of irradiated phosphates of Zr [2] and Ge, the absorption bands of which are in the region 220–320 nm.

Heterogeneous oxidation reactions of naphthalenes have been extensively studied in the presence of V₂O₅ [3] and TiO₂ [4]. Oxidation of naphthalene carried out at high temperature (300–400 °C) gives rise to phthalic anhydride. However, when the reactions are performed in a polar solvent, photo-oxidation products derived from the cleavage of one ring are obtained in good yield only with substituted naphthalenes.

Here we report on the photo-oxidation of naphthalene, 1- and 2-methylnaphthalene and 1-aminonaphthalene under various conditions in order to elucidate the mechanism of the reactions and to optimize the yield of useful products.

2. Experimental details

2.1. Materials

Naphthalene and 1- and 2-methylnaphthalene were pure products (Aldrich). 1-Aminonaphthalene (Fluka) was recrystallized from hexane.

2.2. Catalytic materials

Crystalline α -zirconium hydrogenophosphate, Zr(HPO₄)₂·H₂O (hereinafter ZrPH₂), was obtained by refluxing amorphous ZrPH₂ in 10 M H₃PO₄ for 100 h (ZrPH₂ 10/100) [5]. Crystalline layered germanium hydrogenophosphate, Ge(HPO₄)₂ (hereinafter GePH₂), was prepared by refluxing GeCl₄ diluted with water in H₃PO₄ for 9 h [6]. This compound is isostructural with ZrPH₂ even though it shows a different degree of crystallinity. GePH₂ is more crystalline with a surface area of 4–5 m² g⁻¹, while ZrPH₂ 10/100 exhibits a surface area of 12–18 m² g⁻¹.

2.3. Photoreaction products

All products were identified by gas chromatography (GC) in comparison with authentic samples and analysed by mass spectrometry (MS).

2.4. Physical measurements

Spectra of the acetonitrile solutions of the substrates were recorded with a Hewlett–Packard spectrophotometer.

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Table 1
Photocatalytic oxidation of naphthalenes

Reactant (in CH ₃ CN) (mmol)	Catalyst (mmol)	Irradiation time ^b (h)	Phthalic anhydride (mmol)	Phthalide (mmol)	Phthalaldehyde (mmol)	Naphthoquinone (mmol)
Naphthalene (1.8)	-	14 ^c	0.03			0.01
Naphthalene (0.8)	ZrPH ₂ (0.1)	32	0.3			
Naphthalene (1.8)	ZrPH ₂ (0.1)	32	1.01	0.04	0.01	
Naphthalene (3.8)	ZrPH ₂ (0.2)	40	2.30	0.22	0.01	
Naphthalene (1.8) ^a	ZrPH ₂ (0.1)	34	0.05			Traces
Naphthalene (1.8)	GePH ₂ (0.1)	36	0.40			
1-Methyl- (1.8)	ZrPH ₂ (0.1)	11	0.17 0.05 ^d		0.22 ^e	
1-Methyl- (1.8)	GePH ₂ (0.1)	16	0.06		0.09 ^e	
2-Methyl- (1.8)	ZrPH ₂ (0.1)	13.30	0.09			

^a In benzene; ^b for quasi-total conversion; ^c conversion time of 0.4 mmol naphthalene; ^d 3-methyl-phthalic anhydride; ^e naphthoic aldehyde.

Reflectance spectra of the finely powdered solids were obtained using a Cary reflectance spectrophotometer with MgO in the reference beam.

IR spectra were recorded on a Nicolet 510 Fourier transform IR (FT-IR) instrument.

Gas-liquid chromatography (GLC) analysis was performed in a Varian 3400 apparatus equipped with a silica capillary column (25 m × 0.2 mm) coated with methylsilicone gum. GLC-MS analysis was carried out using an HP 5890 gas chromatograph equipped with a silica capillary column (12 m × 0.2 mm) coated with methylsilicone gum and coupled to an HP 5970 mass spectrometer.

2.5. Thermal analyses

Thermal analyses were carried out by simultaneous thermogravimetry-differential thermal analysis (TG-DTA) in a Stanton STA 801 thermoanalyser.

2.6. X-Ray analyses

X-Ray diffraction (XRD) spectra were recorded with a Seifert XRD 3000 automatic powder diffractometer using graphite-monochromatized Cu K α radiation.

2.7. Photoreactions

The reactions were carried out using the apparatus described in Ref. [1]. The substrate dissolved in 100 ml of solvent (usually CH₃CN) in the presence or absence of the catalyst was irradiated with a high pressure Hg lamp (125 W) in an air stream at 20-22 °C in a quartz or Pyrex (irradiation at $\lambda > 280$ nm) apparatus.

The progress of the reactions was monitored by GLC and GLC-MS measurements. The catalysts were analysed via IR spectra, thermal analyses and XRD spectra at the end of the reactions.

Blank experiments were performed in the absence of light or the catalyst. In the reactions in the presence of ZnCl₂, naphthalene-ZnCl₂ molar ratios of 2 and 1 were used.

3. Results

The irradiation of a suspension of Zr or Ge phosphate in an acetonitrile solution of naphthalene led to various compounds depending on the substrate and reaction conditions. In all cases the cleavage of one ring was observed.

The results are summarized in Tables 1 and 2.

No reaction was observed in the absence of light. Upon irradiating the various substrates without the catalysts, when a tail of absorption of naphthalene occurs in the wavelength region of the lamp emission, partial conversion of the substrates was observed. Their conversion rate is lower than that found in reactions in the presence of ZrPH₂. Moreover, different oxidation products and a lower selectivity were detected as a consequence of different reaction pathways. The photo-oxidation of naphthalene solution in benzene in the presence of ZrPH₂ led to a small amount of phthalic anhydride and naphthoquinone. The irradiation of naphthalene with unfiltered light (2 h) in the presence or absence of the photocatalyst gives rise in the former case to phthalic anhydride (27%) and CO₂ and in the latter case to complete oxidation products.

As we have already observed for alkylbenzenes [1], naphthalene conversion is hindered in the presence of ZnCl₂ only

Table 2
Photocatalytic oxidation of 1-aminonaphthalene

Reactant (mmol)	Catalyst (mmol)	Irradiation time (h)	Phthalic anhydride (mmol)	Phthalimide (mmol)	2-Hydroxynaphthoquinone (mmol)	Naphthoquinone (mmol)
1-Amino- (0.6)	–	5	0.02	0.05	0.02	0.01
1-Amino- (0.6)	ZrPH ₂ (0.05)	5	0.02	0.07	0.02	0.01
1-Amino- (0.3)	ZrPH ₂ (0.05)	5	0.03	0.09		

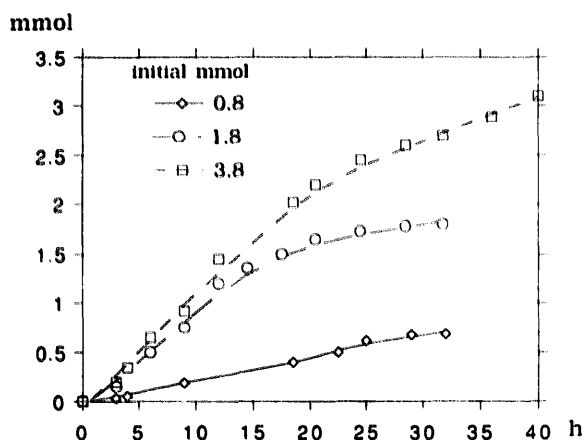


Fig. 1. Conversion of naphthalene at various initial concentrations (0.8, 1.8 and 3.8 mmol in 100 ml CH₃CN) in presence of ZrPH₂.

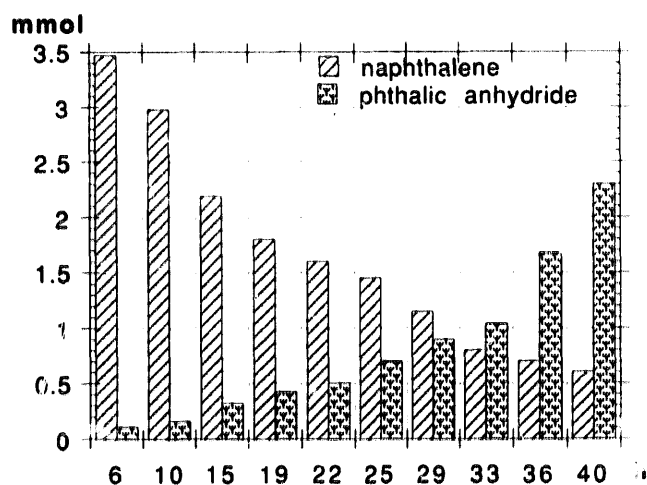


Fig. 2. Variation in amounts of substrate and phthalic anhydride in photo-oxidation of naphthalene (3.8 mmol) in presence of ZrPH₂.

when its amount is comparable with that of naphthalene. When it is lower, we observed the partial conversion of naphthalene and the formation of phthalic anhydride and traces of phthalaldehyde.

The photocatalysed conversion rate of naphthalene depends on the concentration of the substrate (Fig. 1) and on the catalyst (Table 1). Phthalic anhydride is the main oxidation product of naphthalene (yield 70%) when the reaction is carried out on ZrPH₂; its formation as a function of time is shown in Fig. 2. The evolution of CO₂ was observed

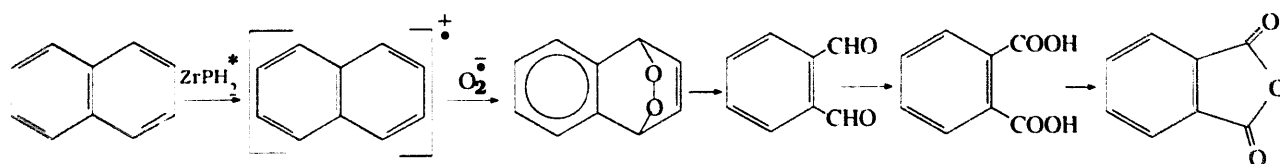
in all cases, but its amount depends on the reaction conditions (substrate, catalyst and their molar ratio).

No difference in the course of the reaction was observed upon using O₂ instead of air. As already observed [1], at the end of all the reactions the catalysts did not show any change in their chemical composition or structure.

4. Discussion

We have already reported on the photo-oxidation of alkylbenzenes in the presence of ZrPH₂ [1] and pointed out the role played by Lewis acidic sites in the course of the reactions. For this reason, initially we have chosen as photocatalyst the more acidic ZrPH₂ 10/100. We assume even in this case (a) an initial interaction of electron-rich molecules of naphthalene with Lewis acidic sites on the surface of ZrPH₂ and (b) an electron transfer from adsorbed naphthalene to excited ZrPH₂ to generate aromatic radical cations. The second hypothesis is supported by the requirement of a polar solvent for naphthalene conversion and the absence of any reaction in the presence of the electron scavenger ZnCl₂ (if present in an amount comparable with that of the substrate). The influence of ZrPH₂ is shown by the following results. Upon irradiating the solution in the absence of ZrPH₂, a tail of absorption of the substrate permits its very slow conversion; only naphthoquinone was detected as an intermediate to phthalic anhydride besides a large amount of CO₂ as a complete oxidation product. The intermediates observed when the reaction is carried out in the presence of ZrPH₂ are phthalaldehyde, phthalaldehydic acid and phthalide. The absence of naphthoquinone indicates that this reaction evolves by a different route from the uncatalysed reaction; in the presence of ZrPH₂ it is reasonable to suppose (the absorption spectra of the inorganic phase are reflectance spectra!) that its molar extinction is greater than that of the substrate in the absorption range 280–300 nm. The results of the reactions performed with unfiltered light, under conditions permitting direct irradiation of the substrate, confirm once more the influence of the photocatalyst: in the presence of ZrPH₂ we observed the formation of phthalic anhydride and CO₂ but in its absence only the evolution of CO₂ was detected.

We propose Scheme 1 to describe the progressive transformation of products in the reaction of naphthalene irradi-



Scheme 1.

ated with light of wavelength greater than 280 nm in the presence of the photocatalyst.

The naphthalene radical cations produced can evolve to endoperoxide by interaction with the activated oxygen species. The formation of endoperoxides has already been observed or hypothesized in the photo-oxidation of substituted naphthalenes sensitized by dicyanoanthracene [7] or in the presence of TiO_2 [4]. The two reactions proceed in different ways, leading to naphthoic aldehyde and acid in the first case and to phthalic acid in the second case.

In the presence of ZrPH_2 the oxidative cleavage of endoperoxide leads to phthalaldehyde, which undergoes further oxidation to phthalic anhydride. No side products of the endoperoxide cleavage were detected. All intermediates were observed in small quantities and this is an indication of the instability of these products under the reaction conditions. Their adsorption on the surface of the Zr phosphate allows their photo-oxidation to phthalic anhydride. In fact, as we previously ascertained, if the photo-oxidation of the substituted aldehydes is carried out under the same reaction conditions but without any catalyst, only the corresponding acid (auto-oxidation) is detected [8].

Very small amounts of maleic anhydride as a secondary reaction product and more consistent quantities of carbon dioxide as an exhaustive oxidation product were observed.

The evolution of CO_2 seems to depend on the decomposition of the oxidized derivatives, because it begins after 2 h irradiation and increases during the reaction as the naphthalene concentration decreases.

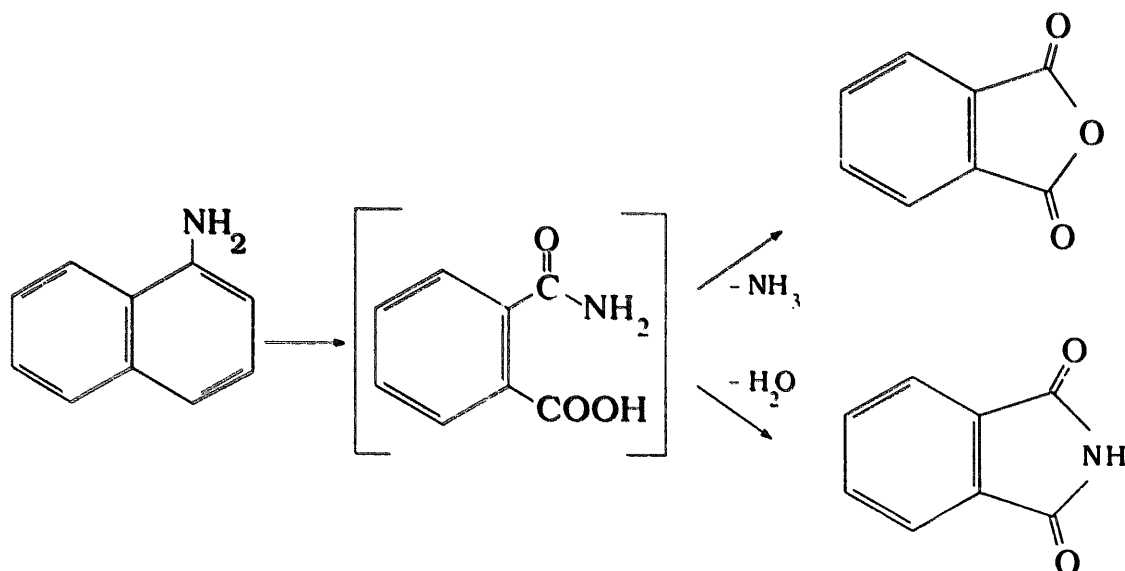
To confirm that the Lewis acidic sites play a very important role in the progress of the reactions, we carried out the photo-oxidation of naphthalene in the presence of GePH_2 ; the conversion is slower than that performed on ZrPH_2 , probably owing to a lower interaction of the substrate with the surface. In previous spectroscopic studies of the adsorption of basic probe molecules on the surface of Zr and Ge pyrophosphates [9] it was found that the Lewis acidic sites, if any, are much weaker in the case of Ge, because their acidic strength decreases with decreasing cationic character of the bonded metal atom on the surface ($\text{Ge} < \text{Zr}$). We assume that a similar trend also occurs in the case of Ge and Zr phosphates.

The conversion rate of 1-methylnaphthalene photolysed in the presence of ZrPH_2 is faster than that of naphthalene. This behaviour can be explained by assuming that the initial electron transfer is favoured in molecules bearing an electron-releasing group.

1-Methylnaphthalene undergoes cleavage of both rings (the ring bearing the CH_3 substituent and unsubstituted ring) in the ratio 3:1.

The regiochemistry of the ring cleavage is consistent with the formation of a radical cation intermediate, since the substituted ring bearing a presumably greater charge and spin density suffers the predominant breaking.

Phthalic anhydride and 3-methyl-phthalic anhydride are the main products obtained from the photo-oxidation of 1-methylnaphthalene (10% and 2.5% respectively), besides small amounts of naphthoic aldehyde; the evolution of CO_2



Scheme 2.

is greater (7.4 mol after 11 h) than that obtained in the photo-oxidation of naphthalene (3.3 mol after 24 h).

The photo-oxidation of 2-methylnaphthalene leads to a low yield of phthalic anhydride and a more consistent production of CO₂ without any detection of intermediate products.

The photo-oxidation of 1-aminonaphthalene has been carried out for two different ratios between the aminonaphthalene and ZrPH₂ and in the absence of the catalyst (Table 2).

Better selectivity of the oxidation products at the end of the conversion is obtained when the substrate–ZrPH₂ weight ratio is 1 or less; the oxidation products are phthalimide and phthalic anhydride.

These compounds certainly derive from the supposed intermediate monoamide of phthalic acid by elimination of H₂O or NH₃ respectively.

Scheme 2 shows the formation of phthalimide and phthalic anhydride.

The formation of the monoamide can be related to that of the monomethylester of phthalic acid detected as an intermediate in the photo-oxidation of 1-methoxynaphthalene to phthalic anhydride [4].

When the substrate–ZrPH₂ molar ratio is 2 or in the absence of the catalyst, phthalimide, phthalic anhydride, naphthoquinone and 3-hydroxynaphthoquinone are formed.

In all the reactions the yield of oxygenated products is low and a large amount of insoluble, coloured powder product is detected besides CO₂.

The various results can be explained by considering that 1-aminonaphthalene shows also in the region 280–360 nm a quite intense absorption band. If the amount of ZrPH₂ is so low that the substrate is not completely adsorbed on its surface, or in its absence, the 1-aminonaphthalene undergoes direct excitation, leading by a radical mechanism to benzoquinone.

In conclusion, in all the reactions an initial electron transfer between the aromatic molecules and the catalyst is observed. The radical ions produced react with activated oxygen to initiate the oxidative cleavage of one ring of the naphthalenes. A good chemical yield of phthalic anhydride was obtained in the photo-oxidation of naphthalene under mild conditions.

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