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The reactions of substituted acyclic 1,3-butadienes on photoexcited TiO_2 in acetonitrile

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Abstract

The reactivities of 2,3-dimethyl-1,3-butadiene, 1,4-diphenyl-1,3-butadiene, 2,5-dimethyl-2,4-hexadiene, and isomeric 2,4-hexadienes in irradiated TiO_2/acetonitrile suspensions were studied. The sterically hindered and conformational restricted dienes appear to be adsorbed at the surface to a lesser extent and/or in a less reactive conformation. The formation of the reaction products is rationalized in terms of hole catalyzed reaction pathways leading to the formation of resonance stabilized radical cations which react with surface adsorbed superoxide anion to yield peroxy radical adducts. Based on the major products it does not appear hydroxyl radicals, even with the addition of water to solvent, can compete with the radical cation reaction pathways under these experimental conditions. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Photocatalysis; Titanium dioxide; Radical cations; Superoxide anion radical; Photooxidation

1. Introduction

There is considerable interest in the mechanistic aspects and the development synthetic applications of radical cation chemistry. A variety of methods, chemical, photochemical, and electrochemical, can be used to generate and study the reactions of radical cations. Bauld et al. have conducted extensive studies on the utility of diene radical cation chemistry toward synthetic applications and have shown chemically generated diene radical cations yield stereospecific Diels–Alder type products [1–5].

Semiconductor photocatalysis in non-aqueous solvents provides a simple means to generate and study the reactions of radical cations [6,7]. Photoexcitation of the semiconductor promotes an electron from the valence band to the conduction band generating an electron (e^-_{cb})/hole (h^+_{vb}) pair. In the presence of an appropriate substrate, electron transfer to the h^+_{vb} can occur to form a radical cation while the conduction band electron is trapped by a suitable e^-_{cb} acceptor. Semiconductors, such as titanium dioxide, can induce oxidation of olefins and aromatic hydrocarbons under oxygen [6–13], and also sensitize isomerization of unsaturated systems [14–19]. A number of different reaction mechanisms, involving hydroxyl radical and hole mediated processes have been proposed to explain these observations, but there is a limited understanding of the role of adsorption on the reaction pathways involved in these semiconductor photocatalysis [6,7,20,21].

TiO_2 photocatalytic generation of radical cations results in the formation of different products then those observed from the photoionization of substrates [22,23]. These observed differences are attributed to the influence of the surface of the TiO_2. In an attempt to develop a better fundamental understanding of the factors governing the reaction pathways of organic substrates on photoexcited TiO_2 we chose to study the reactions of acyclic 1,3-butadienes in acetonitrile solutions. We employed 2,3-dimethyl-1,3-butadiene, 1,4-diphenyl-1,3-butadiene, 2,5-dimethyl-2,4-hexadiene, and isomeric 2,4-hexadienes to probe the reactions catalyzed by photoexcited TiO_2. Our studies suggest that the radical cations are formed on the surface of the semiconductor such that they are stabilized and the addition of superoxide anion radical (not hydroxyl radicals or water) leads to the oxygenated products. Reaction mechanisms are presented to explain the formation of the observed products and rationalize the relative rates of photocatalysis of these acyclic dienes.

2. Results and discussion

We used substituted acyclic 1,3-butadienes as probes to investigate the reactions of diene radical cations generated at

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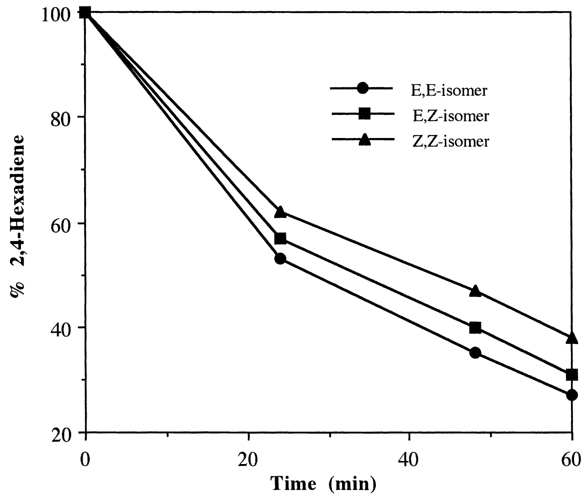

Fig. 1. TiO_2 photocatalyzed phototransformation of isomeric 2,4-hexadienes (7 mM) in oxygen saturated acetonitrile.

the surface of photoexcited TiO_2. Fox et al. have drawn important mechanistic conclusions based on the reaction products for several cyclic and acyclic 1,3-dienes on photoexcited TiO_2 [12]. These elegant studies involve primarily cyclic 1,3-dienes and substrates which would allow for limited conclusions regarding stereochemical and geometrical aspects of the reaction mechanisms [12]. To investigate the influence of stereochemical and conformational factors on the reactivity of the substrate on photoexcited TiO_2, isomeric 2,4-hexadienes were employed as probes. The *cis* and *trans* stereochemistry of the double bonds is not expected to have a significant direct effect on the reactivity of the individual dienes, but the planar cisoid–transoid conformational equilibrium is expected to influence the extent and mode of adsorption and the subsequent reaction pathways.

The relative rates for the photocatalysis isomeric 2,4-hexadienes in acetonitrile are shown in Fig. 1. Control experiments establish that no disappearance of the dienes is observed in the absence of oxygen, light, or the photocatalyst. Surprisingly, the geometric and conformational differences among these isomers had only a modest effect on the relative rates of photocatalysis.

The observed reaction rate of the *E*, *E* isomer is slightly faster than the *E*, *Z* and *Z*, *Z* isomers, this is likely the result of differences in the planar cisoid–transoid conformational equilibrium. The planar transoid conformation is predominant for all the 2,4-hexadienes, but the energy differences between the cisoid and transoid conformations, $\Delta E_{\mathrm{c-t}}$, are significantly different due to steric constraints associated with each isomer. The calculated energy differences, $\Delta E_{\mathrm{c-t}}$, between the planar cisoid and transoid conformers are 2.8, 5.9, and 11.5 kcal/mol for *E,E*-, *E,Z*-, and the *Z,Z*-2,4-hexadienes, respectively [24]. These differences have been used to rationalize the different reactivities of the individual isomers [24–27]. The adsorption ratio of the different conformations is expected to parallel the individual $\Delta E_{\mathrm{c-t}}$ and therefore the *Z,Z* isomer should be adsorbed almost exclusively in the transoid conformation, while the percentage of cisoid conformer adsorbed is greatest for the *E,E* isomer among the 2,4-hexadienes. The faster reaction rate of the *E,E* isomer maybe attributed to faster reactions associated the adsorption of the radical cation in the cisoid conformation (e.g., '4+2' addition of oxygen). Nelsen et al. have reported that specific diene radical cations which can only obtain a cisoid conformation react with oxygen while diene radicals restricted to the transoid conformation do not react with oxygen [28,29]. Steric factors may also play a role in the absolute reactivity of the initial radical cation and overall reaction pathway.

The major products from TiO_2 photocatalysis of the isomeric 2,4-hexadienes in oxygen saturated solutions are acetaldehyde, *cis*- and *trans*-crotonaldehyde, and 2,5-dimethylfuran. The *E,E*, *E,Z*, and *Z,Z* isomers give similar product distributions. The yield of these products determined by gas chromatography is relatively low, acetaldehyde and crotonaldehyde reach a maximum of 22–33% while 2,5-dimethylfuran is between 2–5%. The low yields are not surprising since these products are rapidly oxidized under the experimental conditions. Further oxidation yields products, such as formaldehyde and carbon dioxide, which are lost to the gas phase. Control experiments confirm no reactions occur in the absence of oxygen, TiO_2, or light, but the isomerization of crotonaldehyde takes place under the experimental conditions.

Although numerous investigators propose the addition of oxygen to the radical cations formed during semiconductor photocatalysis, it seems likely that the diene radical cation is formed on the surface of the photocatalyst and subsequently reacts with adsorbed superoxide anion radical[1]. This reaction should occur rapidly given the nucleophilic character of superoxide radical anion and the electophilic character of the radical cation. Once the radical cation is oxygenated it can diffuse from the surface and undergo bond rotations leading to the loss of stereochemical and conformational identities of the peroxy radical adduct. The '2+2' and '4+2' products can be formed via closure of a peroxy radical adduct, yielding the dioxetane and endoperoxide, respectively. The proposed reaction sequence is illustrated in Scheme 1.

These products are unstable under the reaction conditions. Simple cleavage of the dioxetane yields acetaldehyde and crotonaldehyde as products, while loss of water from the endoperoxide yields 2,5-dimethylfuran [25,26,31]. The reactions of singlet oxygen are expected to give similar products, [26] to those observed in these studies, but we consider this

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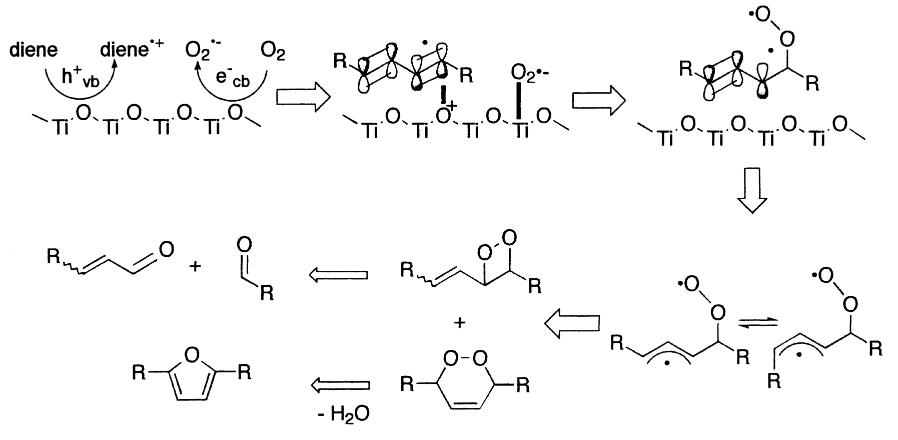
[1] Lew et al. [30] report that conjugated diene radical cations generated photochemically in homogeneous solutions show typical cationic behavior and are insensitive to oxygen. The reactivity of similar radical cations generated on the surface of TiO_2 may be different, but since superoxide anion is much more nucleophilic it is expected to be significantly more reactive towards the diene radical than oxygen.



Scheme 1. Proposed reaction pathways for TiO_2 photocatalysis of acyclic 1,3-dienes.

pathway to be insignificant, since the formation of singlet oxygen during TiO_2 photocatalysis is relatively small[2].

Comparison of relative reaction rates of 1,4-diphenyl-(*E*, *E*)-1,3-butadiene, 2,5-dimethyl-2,4-hexadiene, and 2,3-dimethyl-1,3-butadiene on irradiated TiO_2 suspensions in acetonitrile is shown in Fig. 2. 2,5-Dimethyl-2,4-hexadiene reacts significantly slower than the other acyclic 1,3-butadienes presumably the result of steric hindrance which inhibits effective adsorption of the more reactive cisoid conformation[3]. On the other hand, 2,3-dimethyl-1,3-butadiene reacts the fastest presumably due to the tendency to exist predominantly in the planar cisoid conformation, the most reactive conformation.

The initial reaction rate of the 1,4-diphenyl-(*E*, *E*)-1,3-butadiene is similar to the *E*,*E*-2,4-hexadiene as expected from the geometrical and conformational similarities. Competitive adsorption at the active sites by the reaction products of 1,4-diphenyl-(*E*, *E*)-1,3-butadiene slows the reaction rate at longer irradiation times.

A number of reaction products, formed during the reaction of 1,4-diphenyl-(*E*, *E*)-1,3-butadiene, were identified by mass spectral fragmentation patterns and/or chromatographic comparison with authentic samples. The predominant products[4] are benzaldehyde, benzoic acid, cinnamnaldehyde, cinnamic acid, 2,5-diphenylfuran, 3,6-diphenyl-1,2-dioxene, 2,5-dibenzoylethylene, and 1-phenyl-naphthalene, shown in Scheme 2. Benzaldehyde and cinnamnaldehyde are expected as secondary products of the '2+2' adduct. The aldehydes are easily oxidized to benzoic acid and cinnamic acid under the experimental conditions. The endoperoxide, 3,6-diphenyl-1,2-dioxene was synthesized independently [31] and under the reaction conditions converted to 2,5-diphenylfuran and 2,5-dibenzoyl ethlyene[5]. The formation of 1-phenylnapthalene has been rationalized as a ring closure product (intramolecular Diels–Alder) of the diene radical cation [12]. Radical cation dimers are not observed due to significantly low concentrations of the diene [33].

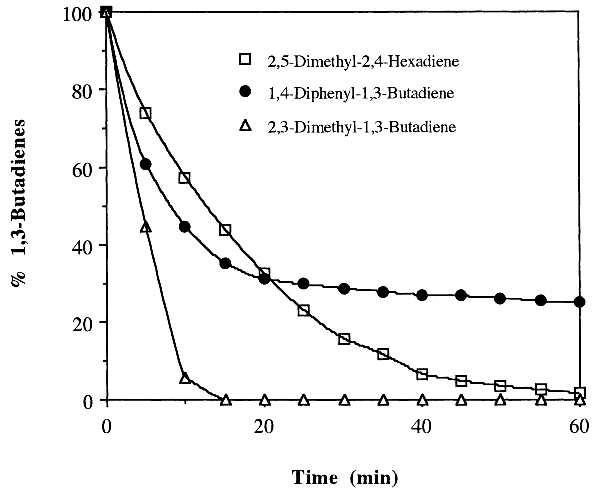


Fig. 2. TiO_2 photocatalyzed phototransformation of substituted acyclic 1,3-butadienes (5 mM) in oxygen saturated acetonitrile.

Analogous product distributions for the different 2,4-hexadiene isomers and the isomerization of 1,4-diphenyl-(*E*, *E*)-1,3-butadiene suggest similar reaction mechanisms involving oxygenation of radical cations, are operative. The

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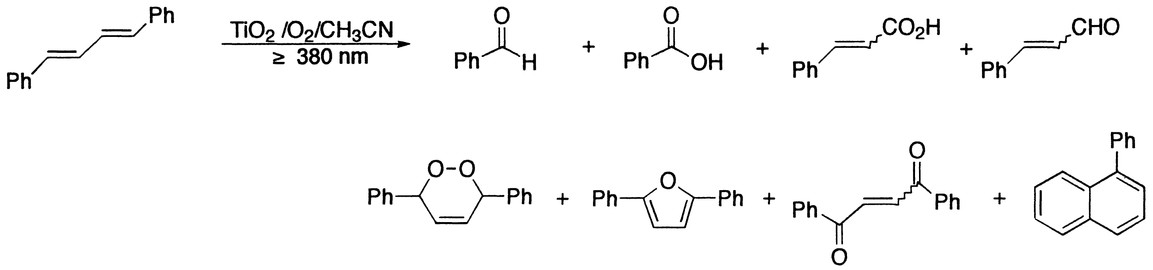
[2] While energy transfer from photoexcited TiO_2 to oxygen and/or electron transfer from superoxide to h_{vb}^+ can potentially lead to the formation of singlet oxygen, no evidence has been clearly established implicating singlet oxygen as being formed in TiO_2 photocatalysis. In addition there was no evidence supporting the formation of the typical 'ene' products expected from singlet oxygenation reactions.

[3] The formation of an usual dimeric product has been reported during photosenitized generation of the radical cation of 2,5-dimethyl-2,4-hexadiene in reference [30]. We were unable to positively identify any of the reaction products due to the large number and low concentrations of products under our experimental conditions.

[4] While photooxygenation and isomerization occur by direct photolysis the rates of these reactions under our experimental conditions (wavelengths >380 nm) are significantly slower than the TiO_2 photocatalyzed reactions. A number of these products have been previously reported in reference [12]. Based on mass spectra tentative assignments are made corresponding to 1,4-diphenyl-3-buten-1-one, 2-benzoyl-benzaldehyde, and dihydro-1-phenylnaphthalene as additional reaction products.

[5] Quantitative formation of 1,2-dibenzoylethlyene has been reported from the 2,5-diphenylfuran radical cation [32].



Scheme 2. Reaction products from the TiO_2 photocatalysis of 1,4-diphenyl-(*E*,*E*)-1,3-butadiene in oxygen saturated acetonitrile.

reaction rates are influenced predominately by the steric and conformational properties of the molecules, while the ease of oxidation diene (peak oxidation potential) and stability of the diene radical cation appear to have a minimal influence on the reactions of these dienes.

In an attempt to promote the formation of hydroxyl radicals via h^{+}_{vb} oxidation of water, 5–10% (~2–5 M) water was added to the reaction solution. Despite this ~1000-fold excess of water relative to the diene the observed product distributions are not appreciable influenced. Although Kodama and Yagi have proposed hydroxyl radical mediated alkene isomerization on photoexcited TiO_2 [19], the intermediacy of radical cation can also be employed to explain their observations.

3. Experimental

3.1. Materials

The 2,4-hexadienes had isomeric purities of >97%. (*Z*,*Z*)- and (*E*,*Z*)-2,4-hexadiene were purchased from Wiley organics. (*E*,*E*)-2,4-Hexadiene, 2,5-dimethylfuran, benzaldehyde, benzoic acid, crotonaldehyde, acetaldehyde, cinnamnaldehyde, cinnamic acid, 1-phenylnaphthalene, and 2,5-dibenzoylethylene were obtained from Aldrich. Acetonitrile, HPLC grade, from Fisher was distilled over CaH_2 prior to use. The gases, oxygen and argon, were UHP grade from Trigas. Degussa supplied the TiO_2 (P25 lot #RV2186). All reagents were used as received unless otherwise noted.

3.2. General procedure

50 ml of 0.005 M solutions of the substituted acyclic 1,3-butadienes in acetonitrile were placed in pyrex reaction vessels. 5 mg TiO_2 was added and the solutions were sonicated for 20 min to produce a homogeneous suspension. The reaction vessels were fitted with air-tight septa and gently purged with oxygen or argon, unless otherwise noted. Magnetic stirring was used to maintain the TiO_2 in suspension during irradiation. 2.0 ml aliquots of solutions were removed at given time intervals. Each sample was filtered with a 0.45 mm PTFE acrodisc to remove the TiO_2 prior to analysis. The controls were subjected to the same procedure and sampling time intervals.

3.3. Instrumentation

Gas chromatographic analysis were performed on a HP 5890 series II Gas Chromatograph instrument equipped with a flame ionization detector and a J&W 0.25 mm × 25 m HP-1 capillary column. Gas chromatography/mass spectrometry (GC/MS) analyses were obtained on a Hewlett-Packard 5791 GC equipped with a 0.18 mm × 35 m DB-5MS column and a mass selective detector. The volatile compounds were analyzed using a J&W 0.25 mm × 100 m HP-1 capillary column. Irradiations were performed in a Rayonet reactor (Southern New England Ultraviolet) equipped with low pressure mercury 'blacklight' phosphor bulbs with appropriate filter solutions and a cooling fan.

4. Conclusions

The relative reaction rates of substituted acyclic 1,3-dienes suggest the planar cisoid conformation produces a more reactive adsorbent. The sterically hindered and conformational restricted dienes appear to be adsorbed at the surface to a lesser extent and/or in a less reactive conformation. While steric and geometrical factors influence the relative reaction rates, similar product distributions among the stereoisomers are rationalized in terms of hole catalyzed reaction pathways leading to the formation of resonance stabilized radical cations which react with surface adsorbed superoxide anion to yield peroxy radical adducts. These adducts can diffuse from the surface and inter-convert through bond rotations to give similar intermediate products. Based on the major products it does not appear hydroxyl radicals, even with the addition of water to solvent, can compete with the radical cation reaction pathways under these experimental conditions.

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