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TiO_2-sensitised photo-oxidation mechanism of indane and some of its hetero-analogues in deaerated CH_3CN

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ABSTRACT: A mechanistic study, principally based on product analysis, relative to the TiO_2-photosensitized oxidation of indane and some of its hetero-analogues, in deaerated CH_3CN and in the presence of Ag_2SO_4, was performed. In particular: (i) 1-acetamidoindan (principal product), indene, 1-indanol and 1-indanone were obtained from indan; (ii) 5-methoxyindan gave 6-methoxyindene (principal product) and 5-methoxy-1-indanone; (iii) 2,3-dihydrobenzofuran, 2,3-dihydroindole and 2,3-dihydrobenzothiophene produced benzofuran, indole and benzothiophen (the last one accompanied by minor amounts of 2,3-dihydrobenzothiophene-1-oxide), respectively. Considering the previous studies on photo-oxidation of analogous substrates as benzylic derivatives (arenes, alcohols and ethers) and from reaction product profiles, an electron-transfer mechanism (from the substrate to the photogenerated hole) is suggested, where the radical cation intermediate should deprotonate to a benzylic radical. The carbocation obtained from the oxidation of this radical should competitively evolve to alkene, alcohol and acetamide. $H_2{}^{18}O$ labelling photo-oxidation experiments suggest that the ketone, when present, should derive from the substrate, through the alcohol as intermediate. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: titanium dioxide; photo-oxidation; indane; radical cation; benzylic radical; deprotonation

INTRODUCTION

The TiO_2 (as powder) sensitised photo-oxidation reaction in CH_3CN can be a useful tool, not only to obtain some mechanistic information about the first (kinetically significant) steps of the photodegradation of organic compounds as pollutants in water,[1] but also to perform a variety of substrate transformations.[2] In any case, it is known that the hole, $(TiO_2)_{h+}$, captures an electron from the organic substrate while the photogenerated electron is transferred to a suitable acceptor (usually oxygen).[2a]

Regarding the second aim (functional group modification), oxygenated products (carbonyl compounds, carboxylic acids, sulphoxides, etc.) are generally obtained in aerated medium;[2a] moreover, the reaction becomes more efficient when Ag_2SO_4 (Ag^+ is the sacrificial electron acceptor) is present in this medium.[2b]

It must be observed that, if this silver salt is used in deaerated medium starting from benzylic derivatives, the process usually maintains its efficiency and less conventional oxidation products are obtained such as dimers,[2c] acetamido derivatives[2d] and ring functionalized products.[2d]

This oxidative process also has the following synthetic advantages: the semiconductor is inexpensive, non-toxic, chemically stable and can be reused after filtration or centrifugation. Moreover, a large number of organic compounds can be oxidised due to the high reduction potential of $(TiO_2)_{h+}$ (2.4 V vs. SCE).[3]

On the basis of the mechanistic information collected for the photo-oxidation of benzylic derivatives, in this paper we report on a mechanistic study, principally based on product analysis, relative to the TiO_2-photosensitized oxidation of indane and its hetero-analogues (all with benzylic structure) in deaerated CH_3CN and in the presence of Ag_2SO_4 (Scheme 1).

RESULTS AND DISCUSSION

The yield and distribution of the products obtained from the photo-oxidation of compounds **1–5** are reported in the Table 1.

In particular, in deaerated medium, **1** gives 1-acetamidoindan, indene, 1-indanol and 1-indanone (entries 1 and 2). Taking into account the previously mechanistic hypotheses regarding the TiO_2-photosensitized oxidation of some classes of benzyl derivatives in this medium,[2d] the steps in Scheme 2 are suggested; in particular, the

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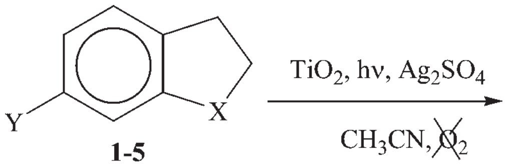


1-5

	1	2	3	4	5
X	CH$_2$	CH$_2$	O	NH	S
Y	H	OCH$_3$	H	H	H

Scheme 1.

cation radical, formed from the substrate through electron abstraction by the photogenerated hole, loses a proton (a process promoted by oxygenated basic sites of TiO$_2$[2e]) from the α-carbon (benzylic site) to give the free radical **10**.

This intermediate is then oxidised to the corresponding carbocation; a second hole should be responsible for this reaction, as observed in the photoelectrochemical oxidation of benzylic alcohols in deaerated CH$_3$CN (two electrons, that is two holes, per molecule are involved).[4]

The fate of the carbocation (Scheme 3) can be suggested considering both the product analysis from **1** and the corresponding profiles of product percent versus reaction time (Fig. 1).

The principal reaction product (Table 1) is the acetamido derivative. The absence of a maximum in the reaction profile (Fig. 1) gives further information: in particular, the acetamido derivative is a reaction product that becomes the principal one after nearly 2 h. This compound should derive from the nucleophilic attack of the solvent on the carbocation through a known pathway (path **a** in Scheme 3).[2d]

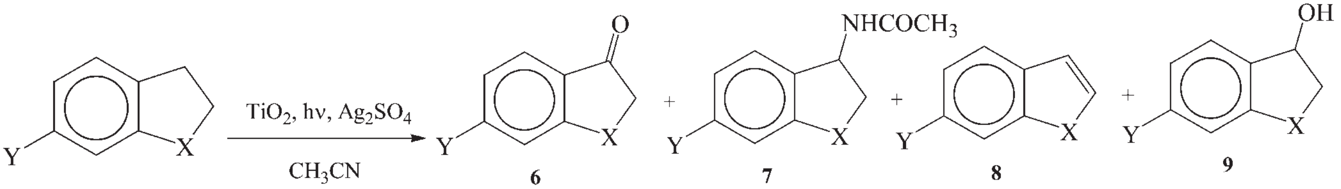
A small amount of indene is also present. The reaction profile of this product shows a maximum in the Figure and indene does not react after an hour when submitted to the same reaction conditions at the same starting concentrations as indane. These results suggest that this cycloalkene is an intermediate obtained through a side equilibrium from the deprotonation of the cation (path **b**).

The profile of indanol, another minor reaction product (Table 1), shows a maximum (Fig. 1); this alcohol, when submitted to the same reaction conditions as indan and at the same initial concentration, gives, as expected,[5] the corresponding carbonyl product (1-indanone). Therefore, indanol is a detectable intermediate that derives from the reaction of the carbocation with H$_2$O[6] (path **c** in Scheme 3), which, in any case, is present in trace amounts on the TiO$_2$ surface.[7]

Indanone is obtained from indanol through the same mechanism previously studied for benzylic alcohols in deaerated CH$_3$CN.[4,5] This reaction should be faster than the photo-oxidation of indane as the alcohol is more efficiently adsorbed at the TiO$_2$ surface; in fact, the adsorption constant of indanol ($K = 380 \pm 100\,M^{-1}$), determined through a Langmuir-type adsorption isotherm,[8] is higher than that of indane, not evaluable by this method ($K < 100\,M^{-1}$).

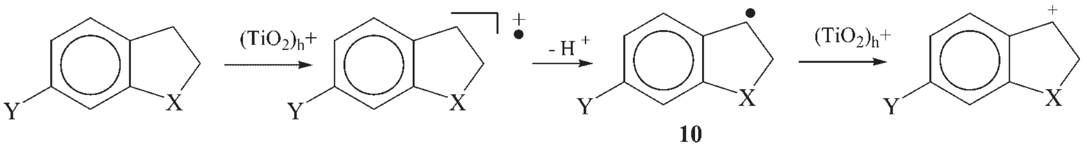
It can be observed from the profile that the amide predominates over the ketone only after 2 h; during this time the molar amount of adsorbed water

Table 1. Product yields in the TiO$_2$-sensitised photo-oxidation of indane and some of its hetero-analoger in deaerated CH$_3$CN and in the presence of Ag$_2$SO$_4$.



Entry	Substrate	X	Y	t, h	Unreacted substrate, %	Product yield, %[a] 6	7	8	9
1	**1**	CH$_2$	H	1.0	66	4	5	2	3
2				3.0	42	8	22	3	6
3				2.0[b]	70	11			
4				2.0[c]	56	26			
5	**2**	CH$_2$	OCH$_3$	1.0	52	11		19	
6	**3**	O	H	3.0	44			37	
7	**4**	NH	H	2.0	71			10	
8	**5**	S	H	1.0	69			13[d]	
9				2.0	40			27[e]	

[a] With respect to the starting material.
[b] In aerated medium without Ag$_2$SO$_4$.
[c] In aerated medium.
[d] 2,3-dihydrobenzothiophene-1-oxide, 5%, is also present.
[e] 2,3-dihydrobenzothiophene-1-oxide, 13%, is also present.



Scheme 2.

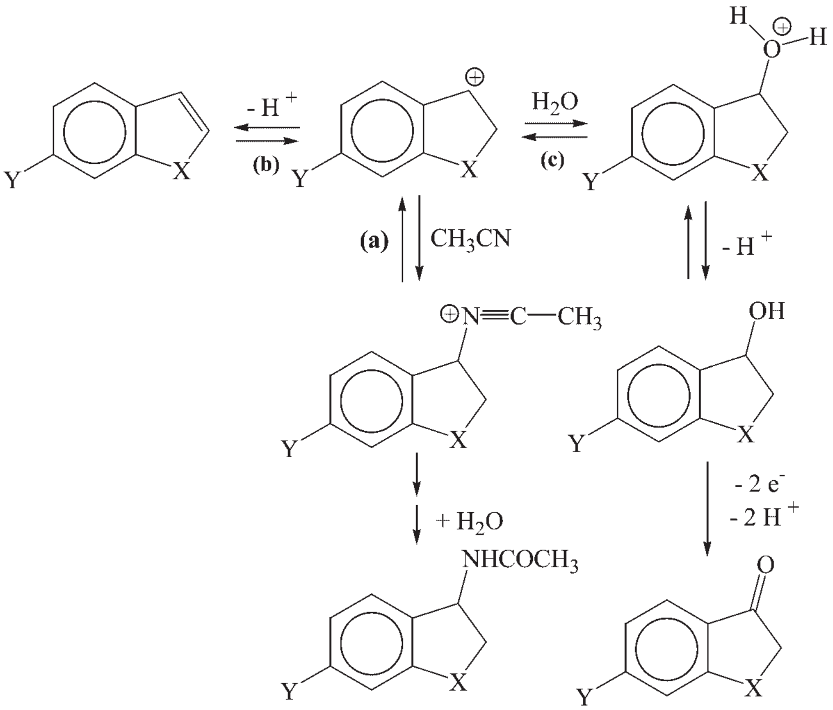
(a better nucleofile than CH$_3$CN) is probably sufficient to compete with the solvent for the capture of the cation (that is, path **c** is able to compete with path **a** in Scheme 3).

A final observation about the profile is that, if the time is longer than 3 h, the amount of alcohol diminishes, the ketone concentration remains practically constant and the amide percent increases. These findings are inline with the reversibility of the alcohol formation that, while the reaction is going on, favours the irreversible process to acetamide.

To acquire further mechanistic information, we have also carried out the reaction starting from **1** in aerated medium; the carbonyl compound (1-indanone, entry 3) is the only product, which is expected based on the results previously obtained from similar cyclic benzylic hydrocarbons.[9] In this medium and in the presence of Ag$^+$, as electron acceptor, the same product is obtained, but more efficiently (entry 4).

According to the previously suggested mechanistic hypotheses on the photo-oxidation of alkylaromatic compounds in aerated medium,[2a,b] the exclusive formation of the ketone represents an evidence in favour of the intermediate **10**. In fact, the radical **10** ($X = CH_2$, $Y = H$) formed as in Scheme 2, in aerated medium reacts very rapidly with oxygen[10] instead of undergoing oxidation to cation; the corresponding peroxy radical then evolves to indanone (Scheme 4).

In line with an electron transfer to the hole as a kinetically significant step (Scheme 2), the reaction from 5-methoxyindan (**2**) is more efficient than that from **1** (compare entries 1 and 5), according to the lower oxidation potential of **2** ($E_p = 1.40\,V$ vs. SCE) with respect to that of **1** ($E_p = 1.97\,V$). In contrast to the reaction from **1**, only two products are obtained from **2**, 5-methoxy-1-indanone and 6-methoxyindene. 6-Methoxyindene is the principal product as it is more stable than indene (in the case of **2**, the equilibrium **b** in Scheme 3 from the carbocation is shifted toward the cycloalkene). A possible explanation for the absence of the 5-methoxy-substituted alcohol (never detected from 0.25 to 3 h) should be that: (i) the alcohol should be oxidized more quickly than 1-indanol to the corresponding indanone (compare the previously measured relative reactivity of 4-methoxybenzyl and benzyl alcohol, $k_{rel} = 24$[5]) and (ii) the alcohol amount formed should be less than that from **1**, because of competition with alkene.



Scheme 3.

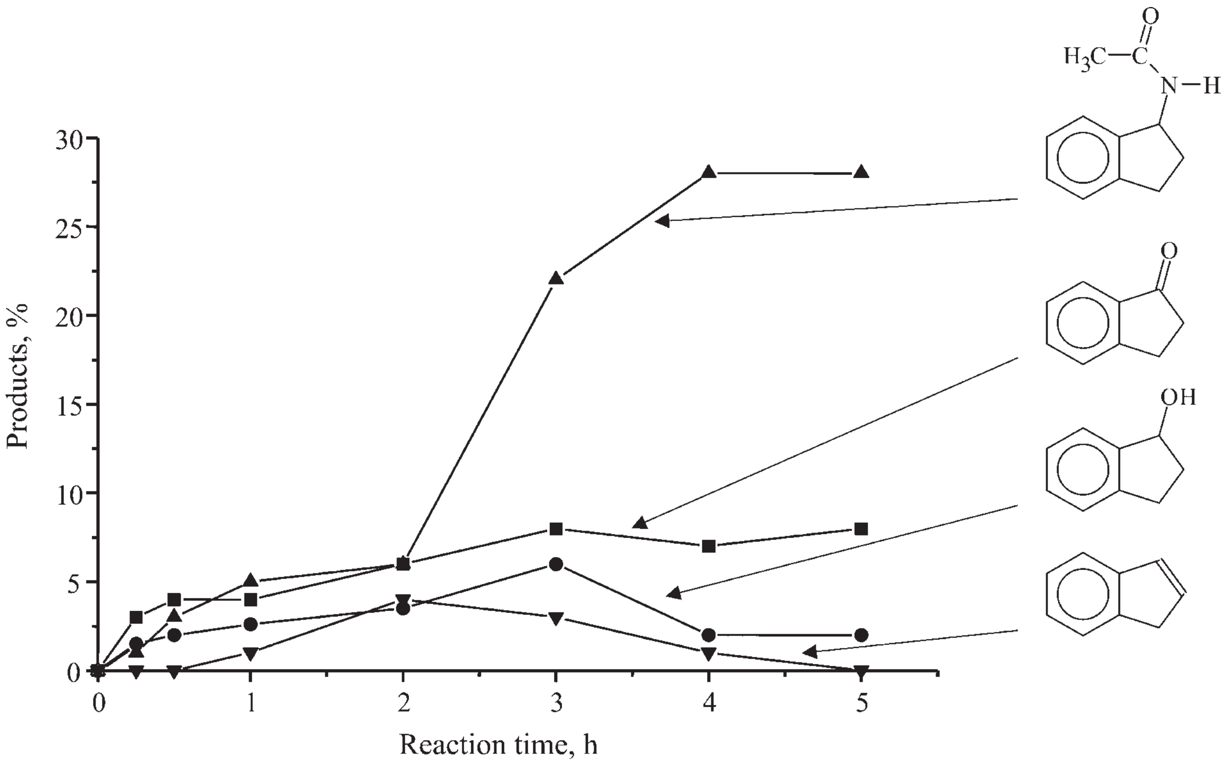
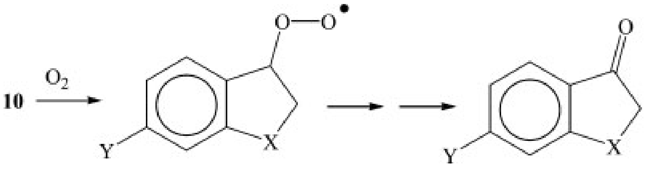


Figure 1. The reaction profile (product percent vs. reaction time) of the TiO_2 sensitised photo-oxidation of indane in deaerated CH_3CN and in the presence of Ag_2SO_4.

To confirm path **c** in Scheme 3, that considers the alcohol as an intermediate even if it was never detected, a labelling experiment was carried out in the presence of $H_2{}^{18}O$. In particular, we observed that ^{18}O (after correction considering the ^{18}O of the labelled water) is completely (100 ± 7%) incorporated by 5-methoxyindanone.

The absence of the acetamido derivative from **2** could be ascribed to the fact that the carbocation in Scheme 3 is more efficiently adsorbed at the semiconductor surface (because of the more effective electronic interaction between the π aromatic system of the substrate, due to the presence of the electron donor OCH_3 group in the ring[11]) than the unsubstituted one; therefore, the first intermediate should preferentially interact with the adsorbed water rather than with CH_3CN (path **c** to indanone is favoured with respect to path **a** to acetamide).

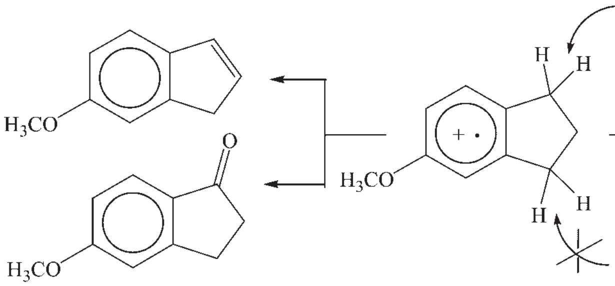


Scheme 4.

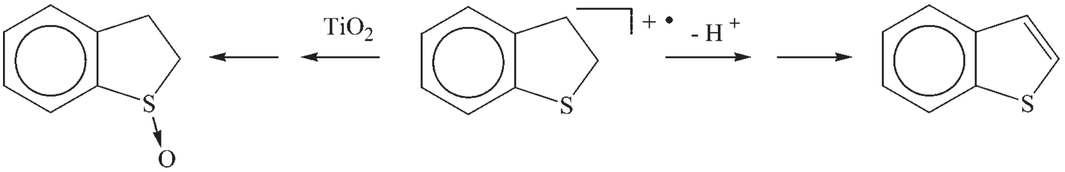
It must be observed that in the $\mathbf{2}^{+\cdot}$ structure, two types of non-equivalent benzylic hydrogens are present (at 1- and 3-C) but, in this reaction, the only one removed from the cation radical is that in the *para*-position (at 1-C) with respect to the methoxy group (only 6-methoxyindene and 5-methoxy-1-indanone are present as products, Scheme 5).

Accordingly the positive charge density in the indan radical cation should be higher at 1-C than at 3-C, as previously reported for 4- and 3-methoxytoluene.[12]

Finally, the only product obtained from 2,3-dihydrobenzofuran (**3**) and 2,3-dihydroindole (**4**) is benzofuran and indole, respectively (entries 6 and 7). Inline with the suggested mechanism in Scheme 3, path **b** should be much more favoured than **a** and **c** in both cases because it yields a bicyclic hetero-aromatic compound that is more stable than the alkenes obtained from **1** and **2**. Also, the aromatization product (benzothiophene) is obtained from 2,3-dihydrobenzothiophene (**5**) but it is accompanied by a minor amount of the corresponding sulphoxide. The product molar ratio from the reaction of **5** is nearly independent of the reaction time (entries 8 and 9). Two parallel reactions, benzylic deprotonation and sulphoxidation[2e] from the radical cation (both induced by the basic centres of TiO_2), should compete (Scheme 6) because a high positive charge density should be localized at the sulphur atom.[13]

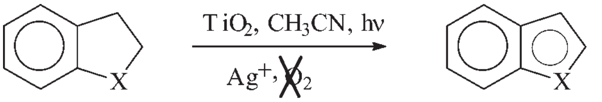


Scheme 5.



Scheme 6.

It must be observed that this reaction can represent a suitable method to aromatize some hetero-cyclic compounds by dehydrogenation in mild experimental conditions (Eq. 1).



(1)

X = O, NH, S

CONCLUSION

From the product distribution and reaction product profiles, the reaction mechanism of TiO_2 sensitized photo-oxidation of indane and its hetero-analogues in deaerated CH_3CN has been proposed. This has been possible as: (i) besides the carbonyl compound (typical of the reaction in the presence of oxygen) peculiar reaction products (acetamido derivative, alcohol and alkene) are formed; (ii) some mechanistic informations had been previously obtained in the study of the photo-oxidation of analogous compounds as benzylic derivatives in the same medium.

EXPERIMENTAL

^{1}H-NMR spectra were run on a Bruker AC 200 (200 MHz) spectrometer, from solutions in $CDCl_3$ with TMS as internal standard. GC-MS analyses were performed on a Hewlett Packard 6890A gas-chromatograph (HP-Innovax capillary column, 15 m) coupled with a MSD-HP 5973 mass selective detector (70 eV). GC analyses were carried out on a HP 5890 gas-chromatograph (HP-Innovax capillary column, 15 m).

Materials

TiO_2 (anatase, Aldrich, 99.9%, dried at 110 °C), CH_3CN (HPLC grade, water content 0.02% from Karl–Fischer coulometry), Ag_2SO_4, indan, 5-methoxyindan, 2,3-dihydrobenzofuran, 2,3-dihydrobenzothiophene, 2,3-dihydroindole, 1-indanone, 5-methoxy-1-indanone, 1-indanol, indene, benzofuran, benzothiophene and indole were commercial samples.

Photochemical oxidation

A solution of the substrate (1.0×10^{-2}M) in N_2- or O_2-purged CH_3CN (20 ml, HPLC grade), in the presence of 130 mg of TiO_2 and of 0.30 mmol of Ag_2SO_4, was externally irradiated using a Helios Italquartz 500 W high pressure mercury lamp (through Pyrex filter), under stirring at room temperature; the oxidation was also performed in O_2-purged CH_3CN without Ag_2SO_4. The TiO_2 powder was then filtered through double paper and repeatedly washed with CH_3CN and diethyl ether; the reaction mixture was poured into NaCl saturated water and extracted with ether. The quantitative analysis of the crude material (substrate + product) was performed by ^{1}H-NMR and by GC with suitable internal standard; the material recovery was generally $\geq$80%. The reaction profile from indan (in deaerated medium and in the presence of Ag_2SO_4) was obtained by GC analysis of reaction samples at different times, after above workup.

Photochemical oxidation of 2 in the presence of $H_2{}^{18}O$

The photo-oxidation of **2**, sensitised by TiO_2, was also carried out in $CH_3CN/H_2{}^{18}O$ (99.5/0.5 v/v). The reaction mixture was analysed by GC-MS. The percent of incorporated ^{18}O in 5-methoxy-1-indanone was determined by the relative abundances of the peaks at *m/z* 162 and 164 $[M^+]$. The percentage of incorporated ^{18}O (corrected considering the ^{18}O content of the labelled water) was $100 \pm 7\%$.

Reaction Products

The products were identified directly from the crude and, if necessary, after column chromatography on silica gel by comparison of ^{1}H-NMR and GC-MS data with those of commercial samples or literature data (for 1-acetamidoindan,[14] 6-metossiindene[15] and 2,3-dihydrobenzothiophene-1-oxide[16])

Cyclic voltammetry

E_p values were obtained from an AMEL 552 potentiostat controlled by a programmable AMEL 568 function generator (at $100\,mV\,s^{-1}$, 1 mm diameter platinum disc anode) in $CH_3CN/LiClO_4$ (0.1 M).

Adsorption equilibrium constants

Equilibrium constants (K) of indanol and indane onto TiO_2 (Degussa P-25, particle concentration $20\,g\,dm^{-3}$) in CH_3CN (HPLC grade) were evaluated using different initial substrate concentrations (C_o) at room temperature (temperature was not controlled because it is reported[9] that K value is not significantly influenced in the range 22–40 °C). The equilibrium concentrations values (C) were obtained (by HPLC) after overnight equilibration of the shaken suspensions and filtration (through Millipore filters) as reported[17]. Each K value corresponds to the average of two determinations.

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