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MECHANISM OF THE PHOTOXIDATIVE CLEAVAGE OF α-METHYLSTYRENE IN DRY MEDIA

J.V.SINISTERRA AND J.M.MARINAS
Organic Chemistry Department.University of Cordoba.Spain

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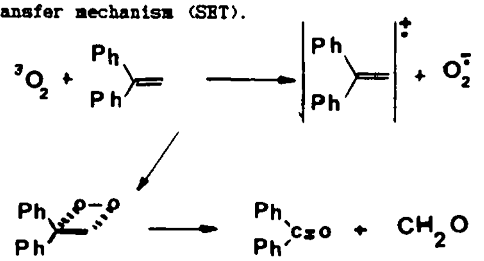
ABSTRACT

The influence of the nature of different active sites on the solid surface is analysed in the photoxidative cleavage of α-methylstyrene (electron-rich olefin) adsorbed on the solid. The process takes place on acid or basic solids giving PhCOCH$_3$ and PhCO$_2$H. Benzoic acid is produced from acetophenone. Selective poisoning experiments of the active sites are carried out in order to determine the nature of the solid surface active sites that act in the process. The Lewis acid-oxidizing sites of the acid solids and the Lewis basic-reducing sites of basic solids are responsible for the photoxidative cleavage of this olefin. These sites seems to be electron carriers in the process.

INTRODUCTION

Photochemical reactions are conventionally studied in homogeneous phases, as far as possible, in ideally stirred media. However, these conditions do not exist in many systems of technical interest. In these cases, the medium can be strongly light-scattering and the reacting species can be very unhomogeniously distributed in it. These facts produce experimental and theoretical complexities. Therefore, the photochemical processes in heterogeneous or dry media have received up to now only moderate attention, which,nevertheless is now growing[1]. However, most of the studies have been concerned with reaction products alone and very few with the excites state of the solid[2].

The photoxidative cleavage of electron-rich olefins with oxygen sensitized by organic compounds[3] or semiconductors[4] takes place by cation radicals. Recently Mazur et al.[5] reported the photoxidative cleavage of 1,1-diphenylethylene adsorbed on SiO$_2$ by air under laboratory light. These authors postulate a contact charge transfer process between olefin and the $^3O_2$ on the surface of the adsorbent. In this process the cation radical from the olefin and the superoxide anion O$_2^-$ are produced by electron transfer mechanism (SET).



It is well known that the activity of solids is related to the solid structure, nature and number of active sites etc.[6,7] by means of steric, electrical and geometrical factors. This fact is not analysed in that interesting paper[5] where the activity of the solids in photoxidation is ascribed to their Brönsted and Lewis acidity.

In order to learn if only the acid solids give the photoxidative cleavage of olefins, we carried out the process on acid and basic solids in a previous letter.[8] In this work we showed that photoxidation takes place both in acid or basic solids. Therefore a more detailed study has been carried out in order to find out more about the role of the solid surface in the process.

Several solids were tested:

-Three amorphous acid solids:i)commercial silica (S) from Merck (Kieselgel 60, 70-230 mesh); ii)$AlPO_4$-SiO_2 (F-72)[9] and iii)$AlPO_4$(F)[10].

-Four microcrystalline acid solids: i)P1 (BPO_4-$AlPO_4$ P/B=1.4; B/Al=1/3)[11]; ii)P2 (BPO_4-$AlPO_4$ P/B=1.4; B/Al=3)[11]; iii)P3 (BPO_4-$AlPO_4$, P/B=1, B/Al=3)[11]; iv)PB (BPO_4)[12].

-Two microcrystalline basic solids :i) C-0 ($Ba(OH)_2$ $8H_2O$) from Probus S.A.; ii)C-200 ($Ba(OH)_2$ 0.2 H_2O)[13]

These solids have different surface area,pore diameter($\bar{dp}$) and pore volume (ΣVp). Furthermore the number of acid , basic and redox sites is different in all cases. Therefore the selective poisoning experiments can give us a good deal of information concerning the mechanism of the process and the role of the solid surface.

RESULTS AND DISCUSSION

1.-Solids

The textural properties of the solids are shown in Table 1. From these results we can say that the amorphous acid solids have larger surface area values and lower pore diameters (dp(Å)) than microcrystalline acid solids as would be expected.

From the powder X-ray diagrams we can deduce that PB is microcrystalline BPO_4. P1 has only microcrystalline $AlPO_4$(the boron compound are amorphous). P2 and P3 are mixtures of several microcrystalline compounds-BPO_4, B_2O_3 ,$Al(PO_3)_3$, $AlPO_4$ according to a previous work[11]. The main crystalline product in P3 is BPO_4. Therefore it is difficult to relate the structure of the active sites to one microcrystalline compound in the cases of P1, P2 and P3 because several compounds, microcrystalline or amorphous, are present in these solids.

The basic solids C-0 and C-200 have the smallest surface area values related to a very regular microcrystalline structure :

C-0 is $Ba(OH)_2$ $8H_2O$

C-200 is $Ba(OH)_2$. H_2O (20% w) on the surface[7]

$\beta Ba(OH)_2$ (80%w) in the bulk of the solid.[7]

The nature and number of solid active sites are shown in Table 1. In the case of acid solids, the number of acid sites versus pyridine (Py) (pKa=5.25) is greater than that of basic sites titrated by means of benzoic acid(BA) (pKa=4.2). On the contrary, in the basic solids the number of basic sites is greater than that of acid sites (these solids have no acid sites with pKa <4.2).[14]

In amorphous solids, silica gel S is slightly more acid (Py/BA=4.6) than F-72(80% SiO_2 - 20% $AlPO_4$) (Py/BA=4). Both solids have higher acid characteristics than F(100% $AlPO_4$) (Py/BA=1.25). This agrees with the fact that $AlPO_4$ increases the number of basic sites in the solids due to the presence of exposed oxygen atoms such as (Al-O(δ)-Al) according to Moffat et al[15].

Table 1

Textural properties and nature and density of active sites (Xm) in solids

Solids	S.area (m^2/g)	$\overline{dp}$ (Å)	ΣVp (mL/g)	Xm ($\mu eq/m^2$)[a]				
				Py	DMPY	BA	DNB	PNTZ
				ACID SOLIDS				
a)amorphous								
S	395	32	0.40	0.73	0.11	0.16	0.02	0.02
F-72	280	35	0.45	1.04	0.02	0.26	0.02	0.07
F	52	30	0.23	2.20	0.04	1.75	0.04	0.02
b)microcrystalline								
P1	23	2605	1.50	1.0	0.17	0.96	0.06	0.003
P2	12	1223	0.53	1.6	0.53	0.54	-[b]	0.03
P3	9	3067	0.69	1.5	0.75	0.35	0.02	0.04
PB	11	810	0.52	28.3	9.7	0.04	0.05	0.04
				BASIC SOLIDS				
microcrystalline								
C-0	1.4	-[c]	-[c]	-[b]	-[b]	40	39	-[b]
C-200	1.9	-[c]	-[c]	-[b]	-[b]	42	14	-[b]

[a] Error ±5%

[b] No active sites of this kind were detected in the solid

[c] No accessible data experimentally due to the low surface area value of the solid

On the other hand the number of acid sites without steric hindrance titrated by the 2,6-dimethyl-pyridine (DMPY) (pKa=7.5) are lower than the one titrated by Py(pKa=5.25). This amount of acid sites diminishes when the $AlPO_4$ percentage increases and the surface area of amorphous solids diminishes as can be expected.

The number of reducing sites titrated by 1,3-dinitrobenzene (DNB) (E.A.=2.2 e.V.) and of oxidizing sites titrated by phenothiazine (PNTZ) (I.P.=7.13 e.V.)is smaller than the number of basic and acid sites -respectively-in all cases. This shows that a great part of the basic and acid sites do not have reducing or oxidizing characteristics, respectively .

In microcrystalline acid solids, PB (100 % BPO_4) is the most acid (Py/BA=707). In other solids,P1,P2,P3 (mixtures of BPO_4 and $AlPO_4$), the greater the ration B/Al, the greater the acid character :

B/Al=3 in P3 (Py/BA=4.3)
B/Al=3 in P2 (Py/BA=3.0)
B/Al=1/3 in P1 (Py/BA=1.0)

Due to the large pore diameter ($\bar{d}$p) of these solids,the number of acid sites without steric hindrance (titrated by DMPY) is greater than in amorphous acid solids.

As in the other cases, the number of reducing and oxidizing sites is similar in all cases.

The basic catalysts C-0 and C-200 are very basic solids because there are no acid sites versus Py. No weak acid sites titrable by cyclohexylamine (pKa=10.6) were detected in these solids in a previous work .

The structure of the active sites of solids is related to the composition of solids.

The Brönsted acid sites of silica are Si-OH[16]. In the case of solids with AlPO$_4$ and/or BPO$_4$, two different kinds of acid sites are described[17]. Brönsted acid sites (P-OH) and Lewis acid sites related to boron or aluminium ions. These Lewis acid sites have oxidizing characteristics.

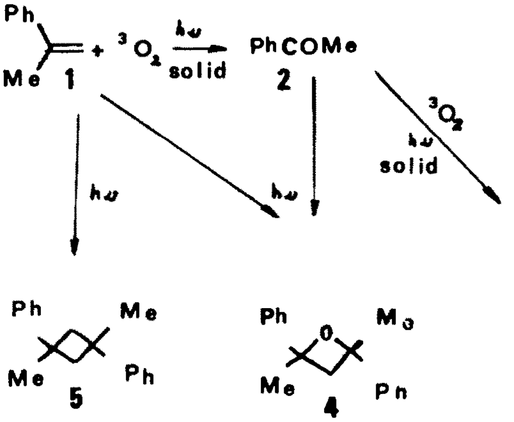
Basic sites are Brönsted (-OH) or Lewis sites (-O- δ^-). The latter have reducing characteristics as well.

In the case of barium hydroxides (C-0 and C-200), the basic sites are related to the superficial OH-[7] . The reducing sites are related to O$^-$ produced by cell lattice dislocations[18]. These sites are Lewis basic sites too.

2.-Photoxidative cleavage

The photoxidative cleavage of α-methylstyrene (1) on the tested solids gave Ph-CO-CH$_3$ (2) and Ph-CO$_2$H (3) as the main products. When the photoxidative process was carried out with great amounts of BPO$_4$ or C-200 (w>0.5g) and very long irradiation times (7 days) new two products were detected by HPLC. These products were isolated from HPLC. 4 (retention time 4.1 ± 0.2 min) and 5 (4.6 ± 0.3 min) were analysed by MS. The formation of these dimerization products 4 and 5 has been described for electron-rich olefins in solution in the presence of oxygen which serves as an electron acceptor .

When 1 was mixed with the tested solids and the samples were stored in the dark, the photoxidative cleavage was not observed.



Scheme 2

In order to avoid secondary reactions, the irradiation time was lowered to 4 days. In these experimental conditions, only 2 and 3 were produced. The results obtained in the photoxidation of 1 are shown in Table 2.

Table 2

Photoxidative cleavage of α-methylstyrene adsorbed on inorganic supports (w=1.0g), Irradiation time 4 days

Solid	molar conversion(%)		selectivity
	$PhCOCH_3$	$PhCO_2H$	to $PhCOCH_3$
	ACID SOLIDS		
a)amorphous			
S	48	24	67
F-72	41	30	58
F	23	13	65
b)microcrystalline			
P1	43	33	57
P2	31	37	45
P3	60	34	64
PB	55	3	95
	BASIC SOLIDS		
C-0	44	33	57
C-200	49	27	64

From these results we can deduce that the photoxidative cleavage of 1, does not only take place in acid solids as postulated by Aronovitch and Mazur[5] ,because the process occurs on basic solids (C-0 and C-200) . Therefore two different mechanisms must be postulated for the process according to the nature of the solid.

In amorphous solids, high surface areas values favour the process (Total conversion X_S > X_{F-72} > X_F) but the selectivity is similar in all cases. The other textural properties, ΣVp and dp,are not important, probably because 1 and $^1O_2$ are very small and no steric restrictions are present.

The acid character of the solid surface seems to be important because the yield in 2 is in accordance with the Py/BA ratio

	S	F-72	F
acid site (Py) / basic site(BA) =	4.6	4.5	1.25
yield in 2(%)	48	41	23

The formation of 3 seems to be favoured by the amount of pure oxidizing sites per gram of solid:

oxidizing site(µeg/g.solid)=oxidizing site(µeq/m^2) x S.area(m^2/g.solid)

Nevertheless due to the very small number of these sites causes,the value show a high degree of experimental error. Therefore this assumption is qualitative.

In the case of microcrystalline acid solids,the surface areas are similar. Therefore this factor cannot control the process as in the amorphous acid solids.

PB is the most selective acid solid to produce 2. This fact could be related to the high Py/BA ratio or to the presence of the BPO_4 microcrystalline structure. P3, with an excess of boron and so with an excess of BPO_4 versus B_2O_3, $AlPO_4$ and $Al(PO_3)_3$, gives good yields in 2 but poorer selectivity than PB because other solids, different than BPO_4 are present and because of P3 has smaller Py/BA ratio than PB. Therefore we are led to think that the microcrystalline structure of BPO_4 favours photoxidative cleavage to 2 and impedes the formation of 3 from 2.

In general, the formation of 2 is favoured by high ratios (Py/BA) because the obtained yield in 2 with P3 is greater than that obtained with P1 and P2.

The yield obtained in 3 is similar in P1, P2 and P3 but the selectivity is greater in the case of P3 according to the greater amount of microcrystalline BPO_4 in P3 than in the other solids.

The microcrystalline basic solids, C-0 and C-200 (with similar number of basic sites versus BA but different numbers of reducing sites versus DNB) give similar conversions in 2 but C-0 gives slightly larger amounts of 3 than C-200. Therefore we can suppose that basic sites are related to photoxidative cleavage to 2 and reducing ones to the formation of 3.

3.-Selective poisoning experiments

In order to learn more about the nature of the active sites of the solids where the reaction takes place, selective poisoning experiments were carried out.

Three representative solids were chosen for these experiments. The strong acid solid PB; the acid-base bifunctional solid P1 and the strong basic solid C-200. The results obtained are shown in Table 3

Table 3

Selective poisoning experiments

Solid	Poison	number of active sites (μeq/m^2 cat)	poison adsorbed (μeq/m^2 cat)*	Xm (%molar)**	
				2	3
BP	-	-	-	55	3
	Py	28.3	30	0	0
	PNTZ	0.04	0.06	6	0
P1	-	-	-	43	33
	Py	1.0	1.0	6	0
	PNTZ	0.003	0.01	4	0
	DNB	0.006	0.01	41	32
	BA	0.96	1.0	39	28
C-200	-	-	-	49	27
	DNB	14	16	0	0
	BA	42	42	5	0

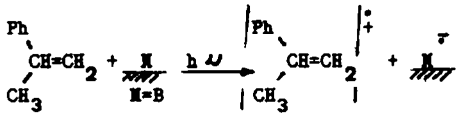
* Error 10%

** mean of three experiments.Error 10% maximum.

In the acid solids, the oxidizing sites with Lewis acid characteristics seem to be responsible for the photoxidative cleavage of 1 to 2 (PB and P1) because these sites are poisoned both for Py and PNTZ give null conversions to 2. The nature of these sites can be related to boron atoms with Lewis acid and oxidizing characteristics.

The synthesis of 3 seems to be controlled by the same sites.

Therefore a mechanism similar that proposed by Mazur et al [5] could be postulated. Olefin 1 is transformed in a cation radical by the single electron transfer process (SET) due to a reaction with a Lewis acid-oxidizing site of the solid:



It is well known that the chemisorption of $^3O_2$ on solids with cations can change the valency such as MoO_3/SiO_2[20,21]; Sc_2O_3[22]; $LaCoO_3$[23] etc. giving superoxide anion O_2^-[21,23]. This species has been detected by EPR in the oxidation of propylene on V_2O_5[23] produced during the adsorption of $^3O_2$ onto the vanadium cations under photochemical conditions.

If we accept the first step, we have a "cation" ($M^{\overset{-}{\cdot}}$ =" $B^{+\cdot}$") that can be oxidized by the $^3O_2$ during chemisorption, regenerating the acid-oxidizing site and giving $O_2^{\overset{-}{\cdot}}$

$$M^{\overset{-}{\cdot}} + {}^{3}\underset{(g)}{O_2} \longrightarrow M \quad O_2^{\overset{-}{\cdot}}$$

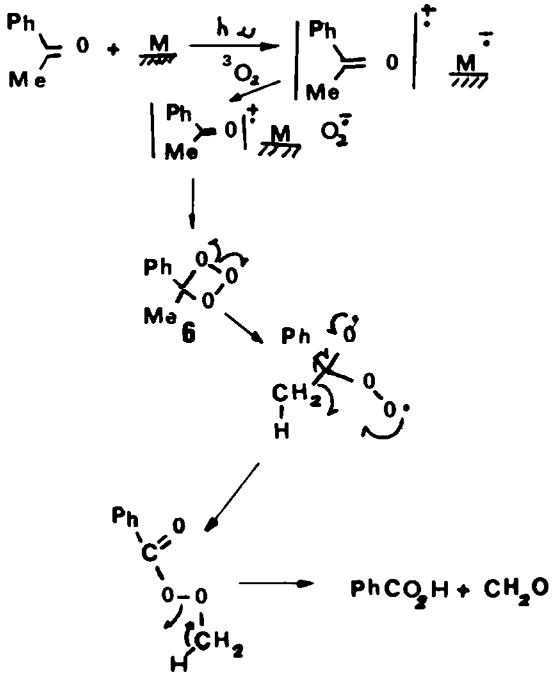
Due to the mobility of the electrons on the solid surface we cannot determine if the same M or a neighbouring one reacts with the oxygen.

This process is well known by the chemists that work in catalysis, can rationally explain the SET mechanism proposed by Mazur et al.[5] and the role of the solid acid sites that is not discussed by these workers in their interesting paper. The recombination of radical ions and the cleavage of the endoperoxide compound are evident steps. (See scheme 1).

We can say that the high selectivity observed with microcrystalline BPO_4 shows that the process is sensitive to the solid microcrystalline structure. Therefore a more detailed study must be done about the role of the crystalline structure in the process by a specialist in surface chemistry.

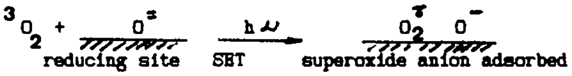
The Lewis basic molecule **2** can be adsorbed on the Lewis acid-oxidizing sites M. Then, a SET is produced by radiation giving a cation radical $\mathbf{2}^{+\cdot}$ and $M^{\overset{-}{\cdot}}$. The production of superoxide anion is carried out in the same way as that discussed above. The photoxidative cleavage of **6** could be explained by a similar mechanism to that we described in our last letter[8].

Scheme 3

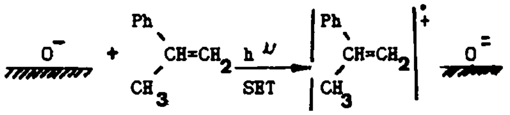


In basic solids,the basic and reducing sites (the only ones titrables by DNB and BA) produce the photoxidative cleavage of 1 as can be deduced from Table 3 because null conversions are obtained when the solids are poisoned by BA and DNB.

In this case we must assume that light activates reducing-basic sites of the solid giving the anion superoxide by SBT during chemisorption of the $^3O_2$ under light. SBT mechanisms catalysed by these active sites have been described by Sinisterra et al. under sonochemical conditions.[25]

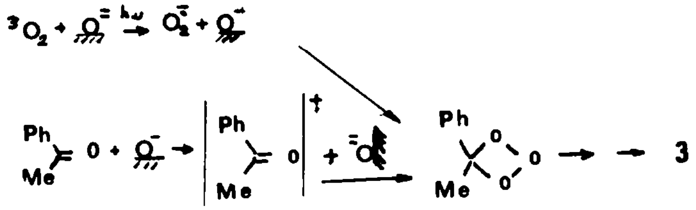


The surface can obtain one electron from the electron-rich olefin giving the cation radical, $1^{\cdot +}$, and regenerating the basic-reducing site.



These radical ions are recombined as shown above giving 2 by the same way.

The transformation of 2 into 3 takes place by a similar mechanism. First step, production of superoxide anion(like above) and second step,formation of PhCOCH$_3^{\cdot +}$ regenerating the active site of the solid. This path way agrees with selective poisoning experiments.



Therefore we encourage organic chemists who work in photochemistry in dry media to analyse the structure and the nature of active sites acting in the process by means of selective poisoning experiments. These sites are essential in the photochemical process as electron carriers. We think that these studies are very interesting from a mechanistic point of view.

EXPERIMENTAL

Solids

a)Amorphous acid solids used were:.-Silica (S) Kieselgel 60, 70-230 mesh from Merk.

AlPO$_4$-SiO$_2$ (F-72) (80% SiO$_2$- 20% AlPO$_4$) was obtained by gelification of AlPO$_4$ on silica (S), according to a method described previously[9] .

AlPO$_4$ (F) was gelified from AlCl$_3$.6H$_2$O and H$_3$ PO$_4$ by addition of NH$_4$OH 1M[10] .

b)Microcrystalline acid solids.-BPO_4(PB) was obtained by direct reaction between H_3BO_3 and H_3PO_4 according to a method described previously.[12]

Three solids, mixture of BPO_4 and $AlPO_4$ were obtained according to these atomic ratios:

P1 (P/B=1.4;B/Al=1/3)

P2 (P/B=1.4:B/Al=3

P3 (P/B=1.0;B/Al=3)

They were obtained mixing H_3BO_3; $AlCl_3.6H_2O$ and H_3PO_4. When the mixture was homogeneous, NH_4OH 1M was added till flocculation. Then the solid was filtered and washed with isopropanol and calcined at 300ºC for 3h.[11]

c)Basic solids.-C-0 is $Ba(OH)_2$ $8H_2O$ from Probus S.A.

C-200 is $Ba(OH)_2$ 0.2 H_2O obtained from C-0 according to the method described previously[13]

Textural and structural properties

Surface area (S.area); pore volume (ΣVp) and pore diameter ($\overline{dp}$) were determined by the B.E.T. method[26] using nitrogen as adsorbent.

The X-ray powder diagrams were recorded in a Philis PW 1130 using filtered CoKα radiation (λ=1.79026 nm). The experimental conditions were: 35kw; 25mA; scanning 15º<2θ<45º;scanning rate 1º.2θ min.

Number of active sites

The number of active sites was determined by a spectrophotometric method described previously[27].Pyrydine(**Py**,pKa=5.2) and 2,6-dimethylpyridine (**DMPY**, pKa=7.5) were used to titrate the acid sites. benzoic acid (**BA**, pKa=4.2) was used to titrate the basic ones. 1,3-dinitrobenzene (**DNB**, EA=2.2 e.V.) and phenothiazine (**PNTZ** I.P.=7.13 e.V.) were used to titrate the one-electron donor and one-electron acceptor sites,respectively.

Selective poisoning experiments

The active sites selective poisoning experiments were described previously[27].Then the poisoned solid was used in the photoxidative cleavage of **1** in the experimental conditions of the reaction.

Photochemical reaction

Photochemical cleavage of adsorbed α-methylstyrene (Merck),1, by oxygen was performed on the described solids. The α-methylstyrene (0.02mL) was adsorbed from the CH_2Cl_2 solution onto the solid (1.0g) and the solvent was evaporated under reduced pressure. Then the dry powder was put in a open vessel under fluorescent light (F40 cool white light. 4x60w; 4x490 lumens), having absorption on set at ca.400nm for four days.

The reaction products were extracted by THF (5mL) and analysed by HPLC (Perkin-Elmer Series 2), using anthracene as the internal standard. $MeOH/H_2O$ (80/20 v/v) as the eluant. Flux=1.2 mL/min., using a $5\mu C_{18}$ column.

ACKNOWLEDGMENTS

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