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INFLUENCE OF THE ACTIVE SITES AND STRUCTURE OF INORGANIC SUPPORTS ON THE PHOTOXIDATIVE CLEAVAGE OF OLEFINS WITH OXYGEN IN DRY MEDIA

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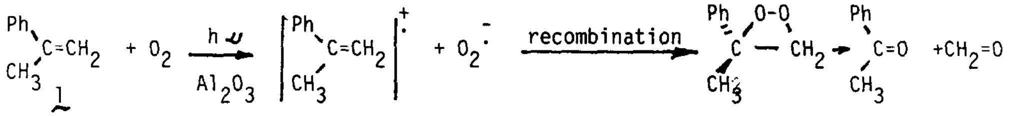
Summary.-The influence of the nature of active sites and the crystalline structure of solids on the photoxidative cleavage of adsorbed α-methylstryrene have been studied.On acid solids,oxidation to $PhCOCH_3$ takes place on electron-ecceptor sites.On basic solids it occurs on electron-donor sites.The microcrystalline solids are more active than the amorphous ones.

Résumé.-La réaction d'oxydation d'alcênes adsrobês sur différents solides a été étudiée.Le processus a lieu sur les centres oxydants dans le cas de solides acides et sur centres réducteurs dans le cas de solides basiques. Les solides avec un reseau cristallin sont plus actifs que les solides amorphes

Catalytic oxidation is an important synthetic method in fine chemical industry.There have been many reports on oxidation cleavage of electron-rich olefins using single oxygen donors as H_2O_2[1],oxygen sensitized by semiconductors[2] or by 9,10-dicyanoanthracene[3],etc.Recently the oxidative cleavage by oxygen of adsorbed olefins has been reported on Al_2O_3,under photochemical conditions[4].The process seems to be carried out by a charge-transfer interaction[4].



The role of the solid is ambiguously discussed by the authors that postulate that the electron-acceptor sites on the solid act as sensitizers in the process that mainly takes place on acid solids[4].

In the present paper,the influence of the nature and number of active sites of several solids on the process is discussed.Three amorphous solids:i)commercial silica(S) from Merck (Kieselgel 60,70-230mesh);ii)$AlPO_4$-SiO_2(F-72)[5] and iii)$AlPO_4$(F)[6];four microcrystalline solids: i)P1(BPO_4-$AlPO_4$,P/B=1.4;B/Al=1/3)[7];ii)P2(BPO_4-$AlPO_4$,P/B=1.4;B/Al=3)[7];iii)P3(BPO_4-$AlPO_4$,P/B=1; B/Al=3)[7];iv)PB(BPO_4) were used as acid solids.Besides,two activated barium hydroxides:C-0($Ba(OH)_2$ $8H_2O$) and C-200($Ba(OH)_2.H_2O$)[9] were tested as basic solids in order to learn more about the influence of the nature of solids in the process.

Photochemical cleavage by oxygen of adsorbed α-methylstyrene(Merk),1,was performed on these solids.The α-methylstyrene (0.02mol) was preadsorbed from the CH_2Cl_2 solution onto the solid and the solvent was evaporated to dryness under reduced pressure.Then the dry powder was

Table 1

Surface area ,nature and density of active sites,X_m,in solids

solids	$S_{area}(m^2.g^{-1})$	$X_m x10^6$ $(eq.m^{-2})$ [a]			
		Py	BA	DNB	PHEN
ACID SOLIDS					
a)Amorphous					
S	380	0.92	0.16	-[b]	0.001
F-72	220	1.41	0.31	0.1	0.001
F	109	0.28	0.02	0.02	0.007
b)microcrystalline					
P1	23	1.0	0.96	0.004	0.013
P2	12	1.6	0.54	-[b]	0.003
P3	9	1.5	0.35	0.02	0.013
PB	11	10.7	0.16	-[b]	0.073
BASIC SOLIDS					
microcrystalline					
C-0	1.4	-[b]	40	39	-[b]
C-200	1.9	-[b]	42	14	-[b]

[a] Error 5%

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

Table 2

Photoxidation of α-methylstyrene,1,adsorbed on organic supports

solids	molar conversion(%)[a]		Selectivity(%)	Molar conversion per m^2 of solid	
	2	3 (wt.cat)	to 2	2	3
ACID SOLIDS					
a)amorphous					
S	48	24(1.0g.)	67	0.126	0.062
F-72	41	30(1.01g)	58	0.187	0.136
F	23	13(1.04g)	65	0.201	0.115
b)microcrystalline					
P1	43	33(0.59g)	57	3.18	2.44
P2	31	37(0.76g)	45	3.42	4.08
P3	60	43(0.79g)	64	8.45	4.76
PB	55	3(1.01g)	95	4.9	0.272
BASIC SOLIDS					
microcrystalline					
C-0	44	33(1.02g)	57	33.5	22.8
C-200	$49._5$	$27._5$(1.0g)	64	26.0	14.4

[a] The values were mean of three experiments (5%)

shaken in open vessels under fluorescent ligh(F40 cool white light,4x60w,4x490 lumens),having absorption onset at ca.400nm during three days.The reaction products were extracted by THF(5mL) and analyzed by HPLC (Perkin-Elmer Serie 2),using anthracene as the internal standard.MeOH/H_2O (80/20 v/v) as the eluent,flux 1.2mL/min. using a $5\mu C_{18}$ column.

The surface area and nature and amount of active sites,X_m(eq.m^{-2}),are shown in Table 1.The surface area was determined by the B.E.T. method.The nature and amount of active sites were determined by a spectrophotometric method described previously[10,11] using several titrating agents.Pyridine(Py pKa=5.25) and benzoic acid(BA,pKa=4.2) were used respectively to tritate the acid or basic sites.1,3-dinitrobenzene(DNB,electron-affinity E.A.=2.21 e.V.)and phenotiazine (PHEN,ionization energy I.E.=7.13e.V) were respectively used to titrate the electron-donor and alectron-acceptor sites.The results obtained are shown in Table 1.

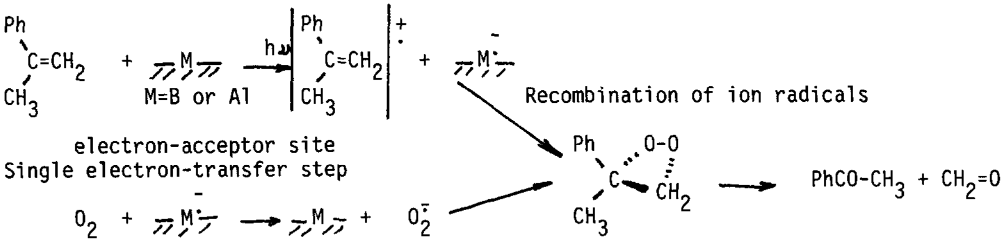
From the results we can deduce that the number of acid sites titrated by Py are greater than that of basic ones with similar pKa,titrated by BA,in the case of solid acids.The strongest acid solid is the boron phosphate,PB,whose density of acid sites (10.7×10^{-6} eq.m^{-2}) is greater than for other solids.Besides this solid has the highest density of electron-acceptor sites versus PHEN.In basic solids,there are only basic and reducing sites but the microcrystalline structure is very different,C-0($Ba(OH)_2.8H_2O$) and C-200($Ba(OH)_2.H_2O$).[12]

When the photoxidative cleavage of 1,previuously adsorbed in these solids,is carried out,acetophenone,2,and benzoic acid,3,were detected by HPLC in all cases.The results are shown in Table 2.No reaction products were observed when the process was carried out in the dark.From the results we can deduce that the photoxidative cleavage of 1,does not only takes place in electron-acceptor or acid sites such as postulated by ARONOVITCH and MAZUR[4],because the process occurs on basic solids (C-0 and C-200) with similar yields and selectivities.Therefore two different mechanisms must be present in the process.

The high surface area values are not important in this case because higher molar conversions per m^2 are obtained with solids with small surface area (P3($9m^2g^{-1}$) or PB($11m^2g^{-1}$)),than with S($380m^2g^{-1}$) or F-72($220m^2g^{-1}$).On the other hand,a microcrystalline structure seems to be necessary to carry out the reaction because higher molar conversion per m^2 to 2,are obtained with microcrystalline acid solids.So,we could sippose a very rigid transition state for the photoxidation with the participation of the cell lattice of the solid.

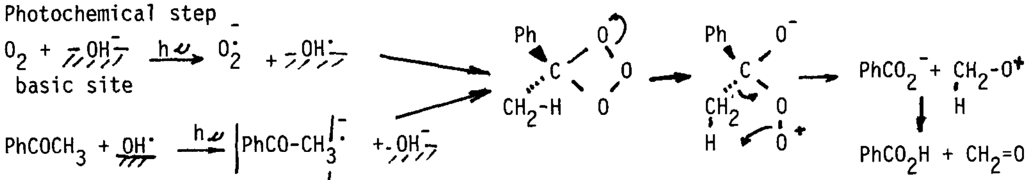
In the case of acid solids small density of basic sites and higher density of electron--acceptor sites seems to be necessary for high selectivities towards the simple cleavage of the olefin to 2 (see PB solid).Therefore we can suppose that the electron-acceptor sites titrated by PHEN are responsibles for the oxidative cleavage to 2 because highest conversions per m^2 and selectivities are obtained with PB and P3.The nature of these sites can be related to boron or aluminium atoms with Lewis acid characteristics.Therefore a mechanism can be proposed with a photochemical first step sensitized by electron-acceptor sites on the solid and with a single electron-transfer step as the second one.This mechanism would be the main path way on the acid solids.

Photochemical step



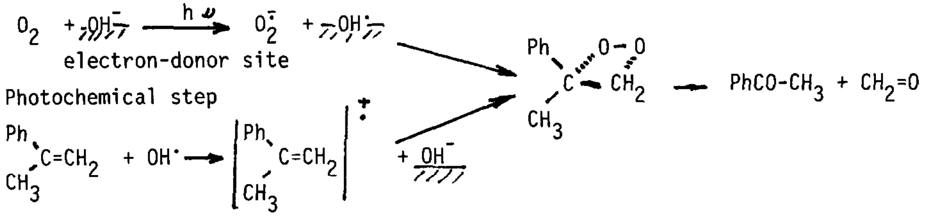
The oxidation of **2** to **3** must occur on the basic sites titrated by BA,because the smaller the number of these sites,the smaller the yield in **3**,with crystalline solids.On the other hand,strong basic solids give high yields per m^2 in **3**.Thus we propose this mechanism for the process,with the basic sites.

Photochemical step



In the case of microcrystalline basic solids[12],C-O and C-200 (with similar number of basic sites versus BA)similar yields to **2**,are obtained(Table 2).Thus,a different mechanism has been proposed in this case where the electron-acceptor sites are not present on the solid surface(Table1).

Photochemical step



3,can be produced by a similar mechanism to that described for the acid solids.

Therefore,we can say that the active sites of the solid support have a very important role in the photoxidation of adsorbed organic compounds and a more detailed study,using selective poisoning agents,is being carried out.

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