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ALKYLATION OF ANIONS ON SOLID INORGANIC SUPPORTS : AN INTERPRETATION OF THE FUNCTION OF THE SUPPORTS

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In the anionic alkylation ($CH_3\ CO_2K + n\ C_8\ H_{17}\ Br$) on solid inorganic supports, silica impregnated with cationic surfactant appears to be as effective as alumina, while silica bearing ammonium groups covalently bonded to the support (SPHEROSIL QMA) exhibits increased effectiveness. An interpretation based upon the superficial charge of the solid surfaces is proposed.

The use of inorganic supports as reaction media in organic synthesis is becoming increasingly widespread (1,2). The effectiveness of various inorganic supports (alumina, silica, clays...) for anionic alkylations has been studied by different groups (3-5) and alumina has generally emerged (3a,4c,5a,b)as the most efficient one for this type of reaction ; to our knowledge, no interpretation of the precise function of the support, based on specific physicochemical parameters has so far been provided. In the present communication, we wish to report preliminary results which indicate that the effectiveness of a support for anionic alkylation (i.e. acetate displacement on 1-bromooctane) depends upon the superficial charge of the solid.

As far as surface charges are concerned (6) alumina exhibits behavior which is different to silica and clays : at the solid-liquid interface with an aqueous solution and in pH conditions at which adsorption of anionic reagents is performed, alumina (7a, b) is positively charged but silica (7b, 8) and clays (9) are negatively charged. Thus electrostatic forces favour adsorption of anions on alumina but not on silica or clays, and this could explain the superiority of alumina over silica and clays for anionic activation.Adsorption of surfactants on alumina or silica is well documented and it is established that cationic surfactants are adsorbed from aqueous solution on silica (and anionic surfactants on alumina) (fig. 1) by initial 1) ion-pairing and 2) ion-exchange (coulombic interactions) followed by 3) hydrophobic interaction of the chains of the incoming surfactant ions with those previously adsorbed (so-called hemimicelles (10) formation). When hemimicelles are formed, the surface exhibits a charge of the same sign as that of the adsorbed surfactant ion, and opposite to its original charge (fig. 1).

In order to test whether a change in superficial charge of the solid support would improve the reaction process, we undertook a study of the influence of the impregnation of solid supports by ammonium salts and surfactants on the reaction of acetate anion with 1-bromooctane. Acetate displacement on 1-bromooctane has been shown to proceed smoothly on alumina (5a) ; we have found that using silica instead of alumina leads to a significantly lower yield, but that impregnation of the silica with quaternary ammonium salts (in catalytic amount with respect to acetate) improves the yield of n-octyl acetate, the best results being obtained with a cationic surfactant, cetyltrimethylammonium bromide (CTAB). In this case, the yield is nearly the same as on alumina. No effect was observed when an anionic surfactant, sodium laurylsulfate (SDS) was used whereas impregnation of alumina with SDS leads to a lower yield of n-octyl acetate (table 1). These results are in agreement with the previously suggested hypothesis that such reactions should be faster on a positively charged surface. One might wonder if the specific role of the quaternary ammonium salts is in fact to induce surface charge modifications or simply to behave as a phase transfer catalyst (11). However $n\ Bu_4\ N^+,\ HSO_4^-$, for which hydrophobic interactions are not important but which is very active as a phase transfer catalyst, is less effective as an additive than CTAB, a typical surfactant, (see table 1).

Table 1. Acetate displacement on 1-bromooctane[a] (at 85°C)

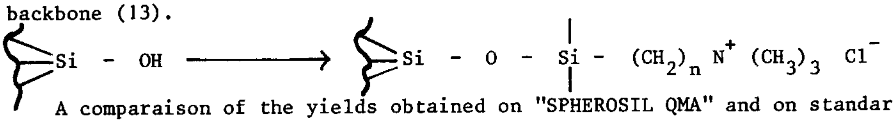
Support	Additive	Time, hr	Yield[h] %	Half-life, hr
Al_2O_3[b]		5	95	1.3
	SDS[f]	"	70	2.6
SiO_2[c]		"	65	2
	n Bu_4N^+, HSO_4^-[f]	"	75	1.5
	CTAB[f]	"	96	0.6
Spherosil[d]			63	3
	CTAB[g]	"	94	0.5
Spherosil QMA[e]		1	100	<0.2
		0.5	88	
		0.25	75	

[a] Impregnated supports are prepared as previously described[5b], but using 1g of CH_3CO_2K adsorbed on 5g on support. Reactions are run without solvent (dry media[5b]) using 4g of impregnated support (6.6 mmole CH_3CO_2K) and 0.67g (3.3 mmole) of 1-bromooctane. With supports impregnated with the ammonium salt of surfactant, the weight of additive is taken into account. [b] Al_2O_3 Merck 90 neutral, 70-230 mesh, pore diameter 90 Å, specific surface area 110 m^2/g. [c] SiO_2 Merck 60, 70-230 mesh, pore diameter 60 Å, specific surface area 500 m^2/g. [d] Spherosil XOB 075, 150-350 mesh, pore diameter 300 Å, specific surface area 100 m^2/g. [e] Spherosil XOB 075 QMA : same characteristics as standard Spherosil[d] with an ionic capacity of 0.66 meq/g. [f] molar ratio

$$\frac{\text{additive}}{CH_3CO_2K} = 0.05.$$

[g] [CTAB] = 0.66 mole/g. [h] Determined from the conversion ratio (^1H NMR) and the weight of collected products ; reproducibility was very good

Morever we supposed that the stronger the interaction between the ammonium groups and the silica backbone, the greater would be the effectiveness of the support. This was confirmed (table 1) by the use of standard "SPHEROSIL" (12) silica as well as the chemically modified "SPHEROSIL QMA" silica caracterised by quaternary ammonium groups covalently bonded to the silica backbone (13).



$$\equiv Si - OH \longrightarrow \equiv Si - O - \underset{|}{\overset{|}{Si}} - (CH_2)_n\, N^+ (CH_3)_3 \quad Cl^-$$

A comparaison of the yields obtained on "SPHEROSIL QMA" and on standard "SPHEROSIL impregnated with CTAB makes obvious the extra effectiveness provided by the covalent bonding of the quaternary ammonium groups.

Further studies aimed at determining other factors influencing the effectiveness of solid inorganic supports are in progress. We are also investigating the use of "SPHEROSIL QMA" silica as a support for other anionic condensations.

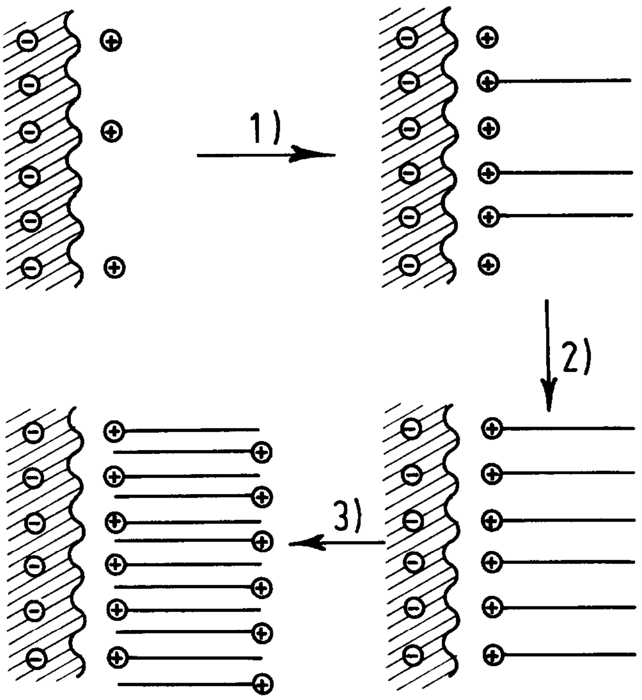


Figure 1 : Adsorption of a cationic surfactant on a negatively charged solid (from ref. 6a and 7b) : 1) ion pairing ; 2) ion exchange ; 3) hydrophobic interactions.

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