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Importance of the Texture of the Resin in Crown Ether Supported Catalysis

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ABSTRACT

The influence of non macroporous and macroporous supports on a test reaction is studied. t-BuOH reacts with tetra O-acetyl bromoglucose in presence of silver nitrate and a supported crown ether. Two reaction products are formed. Yield and selectivity are affected by the morphology of the support. The selectivity depends on the crosslinking degree. This dependence is explained by the rigidity of the matrix and by the variation of steric hindrance.

POLYMER TEXTURE AND REACTIVITY

Polymer supported reagents have received much attention in recent years and found applications in various fields in particular in organic chemistry (KRAUS and PATCHORNIK, HODGE and SHERRINGTON, MATHUR and al., FRECHET, AKELAH and SHERRINGTON, GELBARD).

In early works the supports, commercially available and widely used, were styrene/chloromethyl styrene/divinylbenzene (DVB) copolymers containing 0.5-2% DVB. Such resins were considered as convenient tools and inert solid carriers. However, this point has been questionned and since numerous investigations dealing with the quantitative aspects of polymer supported synthesis have shown that the insoluble support does have a signifiant influence on the reaction. An increasing interest for a better understanding of the relationship between macrostructure, microenvironment, site density and the reactivity of bound species is appearing in the literature (MORAWETZ, SHI-SHYAN PAN and MORAWETZ, TOMOI and FORD, SARIN and al., OHTANJ and al., BRUNELET and al., OKAMOTO and al., KIM and al., BALAKRISNAN and FORD, FORD and al., BERNARD and FORD, DOOLEY and al.).

Supports are now commercially available as beads in a variety of mesh sizes and degree of crosslinking. Beads with < 4% crosslinking are generally considered as gel phases. Resins with higher crosslinking can be macroporous, they differ from the gel phases by the presence of channels or pores even in the dry state (GUYOT, BARTOLIN).

If in homogeneous medium the diffusion of the reactants is generally not the limiting step of the reaction kinetics, this phenomenon may frequently occur with gels, specially with highly crosslinked materials.

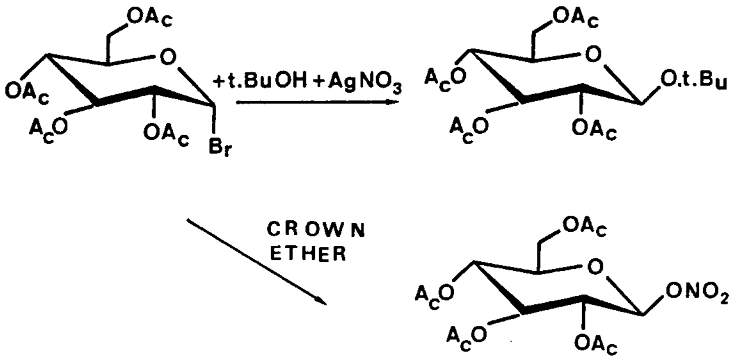
Both for kinetics data and reactivity studies of the supported species it is usual to relate these parameters to classical physico-chemical data of the support such as porous volume (V_p), specific surface area (S_p), DVB content and capacity.

By studying a classical test reaction - the KOENIGS-KNORR reaction - both in homogeneous and supported conditions we will see in this paper that if the classical parameters characterising the structure are relevant, the product selectivity observed is better understood by the chain mobility and steric hindrance of the polymeric framework.

THE KOENIGS-KNORR REACTION

A brominated sugar reacts with an alcohol in presence of a silver, mercury or cadmium salt to form a glycoside. Recent reviews on the formation of glycosidic compounds appeared in the literature (PAULSEN, BOCHKOV, IGARASHI). A macrocycle promotes an anionic activation.

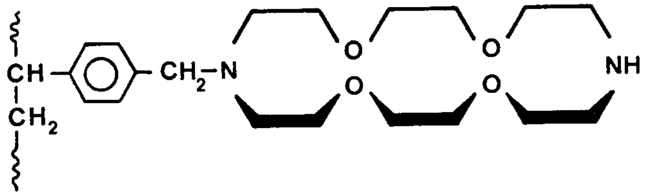
In this case, an acceleration of the reaction results and the formation of a by product (the nitrate ester of the sugar) can be observed depending on the nature of the alcohol and the affinity of the macrocycle for the cation.



As the reaction leads to two products the same run is defined by two parameters yield and selectivity.

In a first paper (RICARD and al.) we have reexamined this reaction in presence of several kinds of free crown ether, polymeric crown ether and crown ether covalently attached to a resin in order to compare the resultant activity of the supported reagent. With the small analogue with t-BuOH and diazatetraoxamacrocycle the reaction leads to a mixture of glycoside and sugar nitrate which is the main product. We show that supported macrocycles increase the glycoside formation. The polymer effect on the selectivity was explained in term of steric hindrance in the vicinity of macrocycle moiety.

In the present work we prepared a serie of styrene/chloromethylstyrene copolymers crosslinked with 0-36% of divinylbenzene by weight. Various macrostructures were obtained and the resins were grafted with the diazatetraoxamacrocycle.



EXPERIMENTAL PART

Synthesis and functionalization of gels

The copolymers of styrene (PROLABO), divinylbenzene (MERCK-Technical product : 50% DVB, 50% ethylvinylbenzene) and chloromethylstyrene (FLUKA - 60/40 meta/para, freshly distillated) were prepared by suspension polymerization in water in presence of benzyl alcohol as diluent (RICARD and al.). All the resins have practically the same chlorine capacity 2.1meq/g.

The grafting of the diazatetraoxamacrocycle (MERCK - K 22) onto the chloromethylated gel was carried out under phase transfer catalysis and already described. Fonctionalized beads with diameter between 100 and 200 µm were selected for the KOENIGS-KNORR reaction. The reaction procedure and the determination of the selectivity are also given in this reference.

Functionalization of linear poly(styrene-chloromethylstyrene)

To a solution of poly(styrene-chloromethylstyrene) (1.5g) in 30cm^3 of dry dimethylformamide (DMF) are successively added triethylamine (1cm^3, 10 min. of stirring) and diazatetraoxamacrocycle (1g) in 5cm^3 of methylene chloride. The reaction mixture is stirred 2 days at room temperature and then acidified with dilute HCl. DMF is evaporated under high vacuum. The slurry is poured in water. The precipitate is isolated by filtration, washed with water and dissolved in methanol. The alcoholic solution is poured in vigourously stirred dilute NH_4OH. The polymer is recovered by filtration, washed with water and dried. The crude product is dissolved in CH_2Cl_2, then filtrated through a 0.5μ membrane and the filtrate evaporated. 1.6g of polymer are obtained.

Characterization of the resins

Both chloromethylated beads (TABLE I) and grafted resins (TABLE II) were studied.

Apparent densities were determined by weighing a given volume of the dry resins in a graduated pipette.

The texture of the beads was characterized in the dry state by porous volume and surface area from nitrogen adsorption/desorption following the BET method. In fact the porous volume is conveniently measured by this technique only for small pores. Distribution of large pores (diameter more of 100nm) was obtained using mercury porosimetry (Apparatus CARLO ERBA) (GREGG and SING). This latter method is not valid for resins with small pores or poor rigidity.

In the swollen state resins were also charaterized by change of the apparent volume of a given weight of beads in presence of methylene chloride.

RESULTS AND DISCUSSION

In homogeneous conditions with non supported species the test reaction carried out either in pure t-BuOH or with added CH_2Cl_2 leads to a mixture of the glycoside derivative (7%) and the nitrate one (93%). In all cases the yield, regarding the sugar, is quantitative.

When the macrocycle is attached to a styrene/divinylbenzene structure the glycoside formation increases. We found that the capacity of the resins, in the range 0.2-0.5meq/g, has no influence on the chemical yield and the selectivity. So results regarding the influence of parameters such as V_p, S_p or DVB content can be obtained by comparing resins of different K 22 capacity.

TABLE 1

INFLUENCE OF CROSSLINKING DENSITY ON CHLOROMETHYLATED RESIN PROPERTIES

% DVB	Cl meq/g	swelling ratio[a]	apparent density g/cm^3	Vp[b] cm^3/g	Sp[b] m^2/g
1	2.1	8.1	0.55	∿ 0	∿ 0
2	2.1	4.5	0.50	0.05	20
5	2.2	3.1	0.50	0.1	50
10	2.2	2.1	0.3	0.1	60
20	2.1	1.7	0.2	0.15	100
36	2.1	1.1	0.3	0.30	165

a) swollen volume in CH_2Cl_2 by dry volume.
b) determined by BET nitrogen adsorption.

TABLE 2

INFLUENCE OF CROSSLINKING DENSITY ON RESIN PROPERTIES

% DVB	Graft meq/g	swelling ratio[a]	apparent density g/ml	Vp[b] cm^3/g	Sp[b] m^2/g	V[c] cm^3/g
1	0.5	3.5	0.6	∿ 0	∿ 0	∿ 0
2	0.2	2.7	0.6	∿ 0	∿ 0	∿ 0
5	0.5	2.2	0.40	0.1	40	0.49
10	0.5	1.7	0.30	0.1	40	0.72
20	0.35	1.35	0.30	0.17	90	0.66
32	0.5	1.4	0.30	0.30	180	0.69
36	0.18	1.1	0.30	--	--	--

a,b : see TABLE 1. c : mercury porosity.

Chemical yield

On figure 1 is plotted the chemical yield versus the crosslinking density. In t-BuOH, which does not swell polystyrenic gels, the yield of the reaction is about 95% with resins of low DVB content, it slightly decreases with increasing crosslink. The role of the resin morphology on the activity of a supported catalytic site has already been discussed (FORD and al). Generally resins with large specific surface areas give better results. But, here, it has not a major effect since an increase of this parameter from 0 to $180m^2/g$ leads to a slight yield decrease. This suggest that in our experimental conditions the mobility of the reactive sites plays and important role and a decrease in the chain flexibility has a negative effect on the diffusion ability of the reactants (t-BuOH-$AgNO_3$) in the bulk gel and consequently on the global reaction kinetics. This idea is reinforced by the experiments runned with a swelling solvent like CH_2Cl_2 : the diffusion of reactants is improved and the yield reaches 100% whatever the resin (fig. 1).

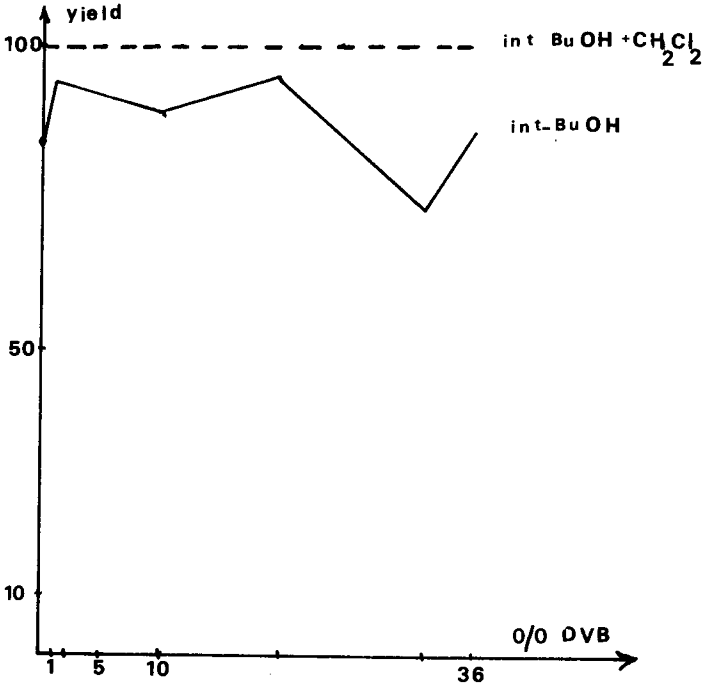


Fig. 1 : Variation of the yield with % DVB.

Selectivity

In t-BuOH the nitrate/glycoside ratio is nearly constant whatever the specific surface area or porous volume of the supports for various DVB content (fig. 2). The classical physico-chemical parameters do not appear as convenient keys to explain these results.

In methylene chloride the evolution of the selectivity is very similar to the swelling (fig. 2 and 3). These experiments suggest, as precedently proposed a reaction mechanism involving a competition between the two nucleophiles t-$BuOH^-$ and NO_3^- at the glycosidic center. An high rigidity of the matrix restricts the mobility of the macrocycle which acts as a screen for the associated NO_3^- ion. Consequently the reaction with t-BuOH, in excess, is favoured. The larger the rigidity of the matrix (provided by an increase in DVB content or/and the use of a bad swelling solvent), the larger the yield in glycosidic derivative is.

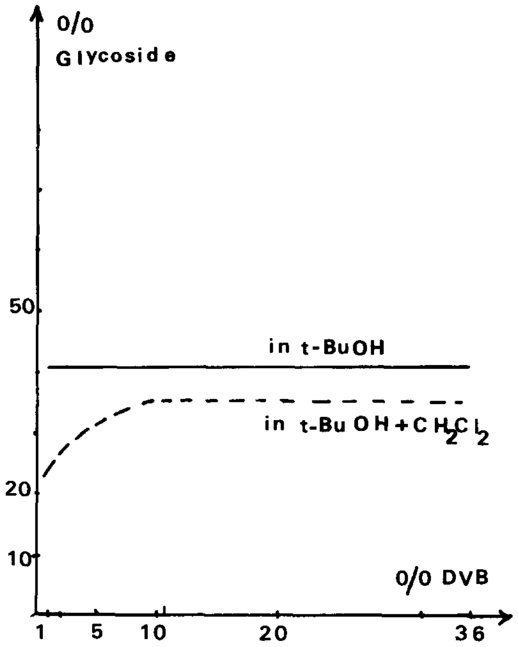


Fig. 2 : Variation of the selectivity with % DVB.

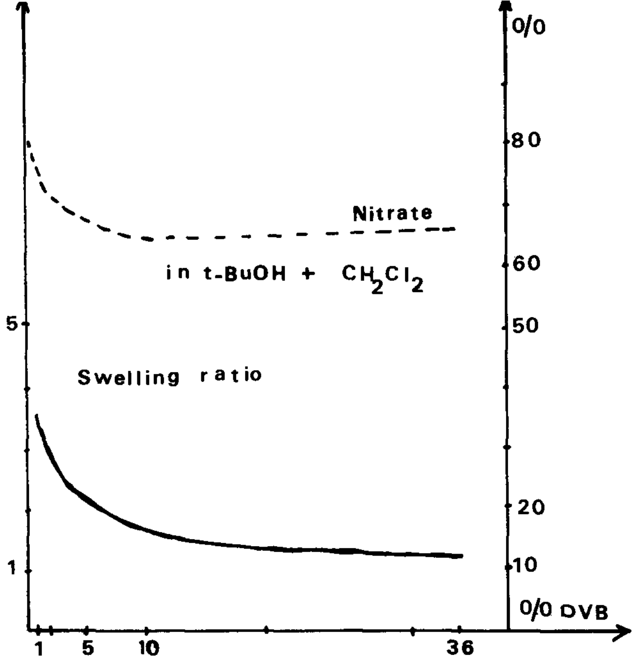


Fig. 3 : Swelling ratio variation with % DVB and % Nitrate with % DVB.

CONCLUSION

If classical parameters like specific surface area are more than likely relevant to describe the behaviour of rigid supported catalysts, with active sites only on the surface of the support, additional data must be used if the reactive species are part in the bulk support and if it can swell.

In the case of the KOENIG-KNORR reaction in presence of supported tetraoxamacrocycle bound to a styrenic resin the evolution of the chemical yield and the selectivity can be explained according to a steric hindrance due to the rigidity of the chains.

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