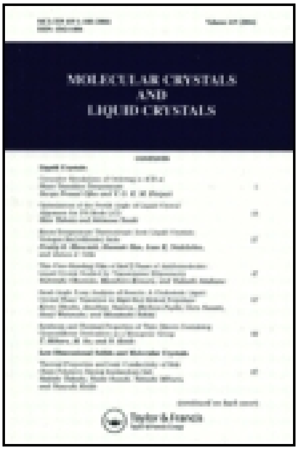

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# An Organic Solid State Reaction: Alkylation of Aromatic Solid Substances by Alkenes and Solid Catalysts

Roger Lamartine [a], Fouad Lamsouber [a] & Robert Perrin [a]

[a] Université Claude Bernard Lyon I, Laboratoire de Chimie Industrielle, UA 805. 43, Boulevard du 11 Novembre 1918, 69622, Villeurbanne, Cédex, France

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# AN ORGANIC SOLID STATE REACTION : ALKYLATION OF AROMATIC SOLID SUBSTANCES BY ALKENES AND SOLID CATALYSTS.

ROGER LAMARTINE, FOUAD LAMSOUBER and ROBERT PERRIN
Université Claude Bernard Lyon I, Laboratoire de Chimie Industrielle, UA 805. 43, Boulevard du 11 Novembre 1918, 69622 Villeurbanne Cédex, France.

Abstract Catalyzed alkylation of solid aromatic substances is envisaged. The solid phenol, isobutene gas reaction is carried out in the presence of solid catalysts. Two phosphoric acid and silica based catalysts were prepared and tested. The reactivity and selectivity of the solid phase reaction were determined as a function of the nature and quantity of the catalyst. The results are compared with those of the liquid state and the solution. A mechanism involving transfer of active entities from the solid catalyst to the solid organic reagent is proposed.

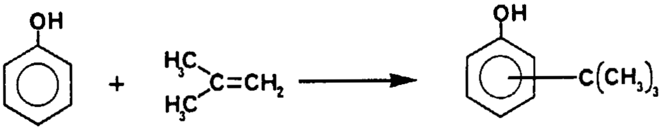
## INTRODUCTION

Alkylation of aromatic substances has been thoroughly studied in the liquid phase, in solution and in the gaseous phase [1,2]. Very few studies take solid reagents into account [3].

For those reactions numerous catalytic systems have been devised, as for example catalysts of the Friedel-Crafts type, organic acid catalysts and mineral acid catalysts such as $H_2SO_4$, HF, $H_3PO_4$. Phosphoric acid based catalysts have the advantage of not giving polysubstitution or polymer derivatives [4].

Taking into account the results previously obtained during hydrogenation of aromatic solids in the presence of metal catalysts[5], we sought to bring about alkylation of the solid aromatic substances in the presence of a phosphoric acid based catalyst.

The reaction that was studied was that of solid phenol exposed to the effect of isobutene gas in the presence of phosphoric acid.



To carry out this reaction in the solid state, we were obliged to prepare solid catalysts, because the phosphoric acid and the phenol do not give products in the crystalline form.

## EXPERIMENTAL

The solid state reactions were carried out at 30°C and at 760 torr alkene pressure. The phenol is ground to a fine powder and mixed with the solid catalyst powder.

### Preparation of the catalyst

10g. of phosphoric acid, with a molar ratio, $P_2O_5/H_2O$ = 0.33 was obtained by adding phosphoric pentoxide, $P_2O_5$, to orthophosphoric acid $H_3PO_4$, $P_2O_5/H_2O$ ratio = 0.2

are mixed with 3.9 g of silica gel (MERCK, particle size, 0.063-0.200 mm, pH = 7)

The mixture is brought to a temperature of 195°C for 2 hours under a $10^{-3}$ torr vacuum. The solid thus obtained is reduced to fine powder by mechanical grinding.

## Characterisation of the catalyst

The solid catalyst in powder form was characterized by its X-Ray spectrum. The spectra were obtained by using a SIEMENS D-500 automatic diffractometer equipped with a system to process the results, using the DIFFRAC 11 program on a PDP 11 calculator, and the possibility of phase search on JCPDS files. The diffractometer equipped with a rear monochromator used copper K$\alpha$ radiation ($\lambda$ = 1.5418 Å).

The X-ray spectrum shown in Figure 1 corresponds to a powder obtained following the process described above. The X-ray spectrum of Figure 2 corresponds to a powder which has undergone an additional calcination treatment in air, heated at the rate of 150°C/hr for 4 hours.

Catalyst A, Figure 1, presents an amorphous part and a crystalline part. Catalyst B, Figure 2, is a very highly crystallized product.

The identification of the spectra, Figures 1 and 2, lead to attributing to catalyst A the formula : $Si_3(PO_4)_4$ , ($3SiO_2$- 2 $P_2O_5$), which is a neutral orthophosphate probably mixed with another form of monoacid orthophosphate : $Si(HPO_4)_2$ ($SiO_2$-$P_2O_5$-$H_2O$), as conforms with the studies by BOULLE and al[6,7]. The catalyst B would be biphasic and composed of neutral orthophosphate $Si_3(PO_4)_4$ ($3SiO_2$-$2P_2O_5$), and neutral pyrophosphate $SiP_2O_7$ ($SiO_2$-$P_2O_5$).

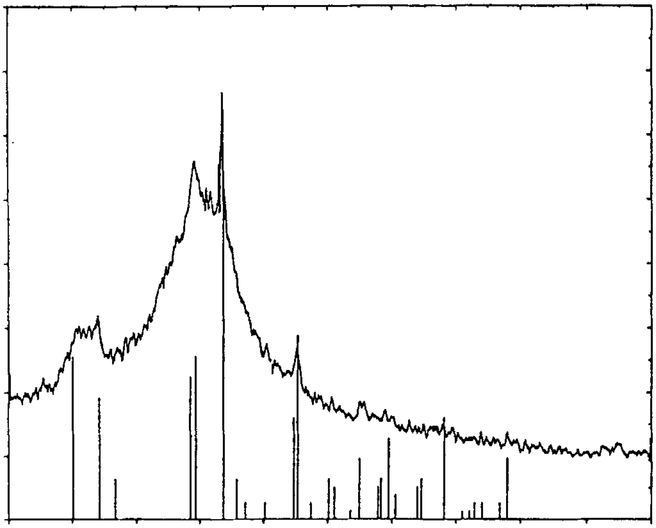


FIGURE 1. X-Ray spectrum of catalyst A

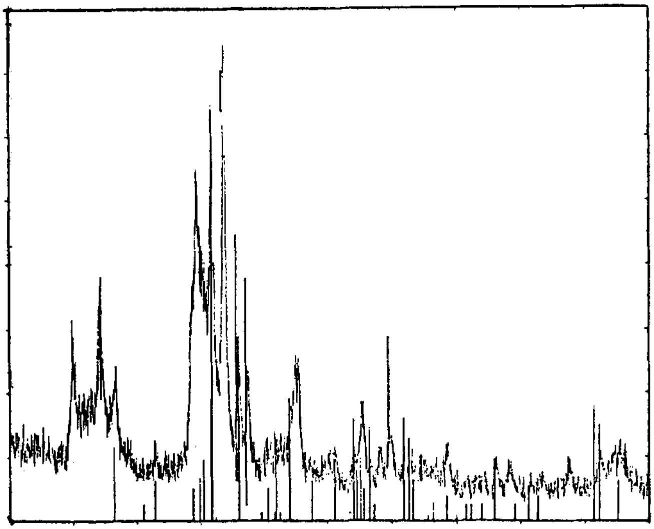


FIGURE 2. X-Ray spectrum of catalyst B

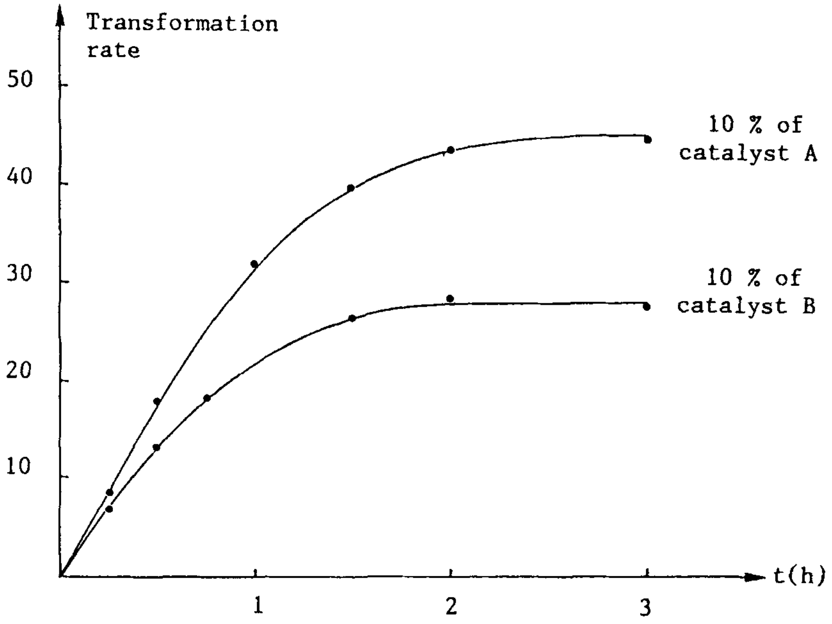


FIGURE 3. Catalytic activity of A and B

## RESULTS AND DISCUSSION

The dependence of the reactivity and selectivity of the alkylation on the nature and quantity of catalyst was successively studied. The results were compared with those obtained in the liquid state and in solution.

### Influence of the nature of the catalyst

Two catalyst A and B were studied. The results obtained are illustrated in Figure 3, showing that the reactivity in the solid state depends on the nature of the catalyst. The fact of calcinating the catalyst notably decreases its reactivity. The calcination brings about a change of phase and leads to the formation of neutral pyrophosphate $SiP_2O_7$ by dehydration of the hydrated orthophosphate $Si(HPO_4)_2$ present in the catalyst A[8]. Thus the less active catalyst B, consisting of neutral orthophosphate and pyrophosphate is deprived of water. The activity of the catalyst therefore is linked to the amount of water it contains.

This results is to be compared with that obtained in the polymerization of olefins using a catalyst of the same type , known by the name "UOP catalyst". In this reaction P.H. EMMET[9] and also E. WEISSANG and P.A. ENGELHARD[10] were able to show that it is the water vapour tension which reigns above the catalyst that regulates its activity.

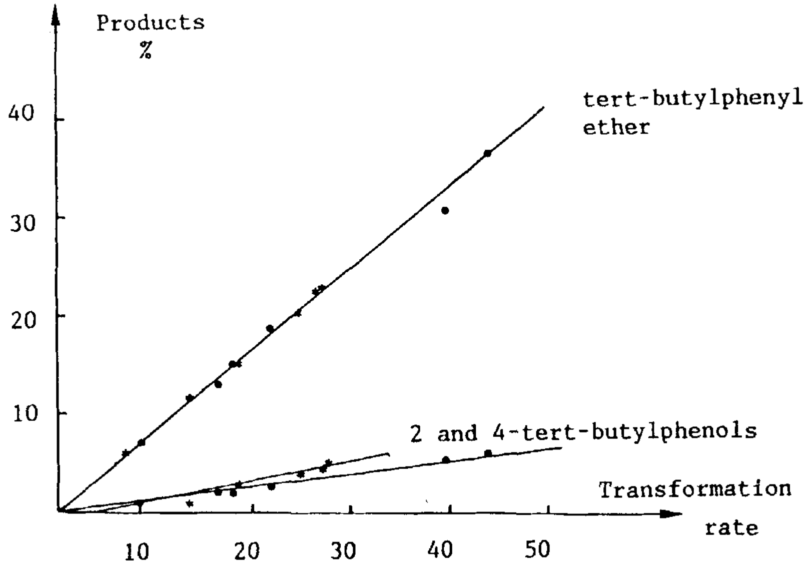


FIGURE 4. Composition of the obtained products versus transformation rate .● catalyst A ; * catalyst B

In the course of this reaction of alkylation in the solid phase, tertiobutylphenylether is essentially the product formed. The composition of the products formed as a function of the transformation rate is given in Figure 4 which shows that the nature of the catalyst does not notably modify selectivity.

We should also point out that the tertiobutylphenylether is a liquid product under the reaction conditions. As the rate of transformation increases, the liquid phase becomes proportionally greater and tends to decrease the reactivity, as is shown by the levels obtained beyond 1.5 hr of reaction given in Figure 3.

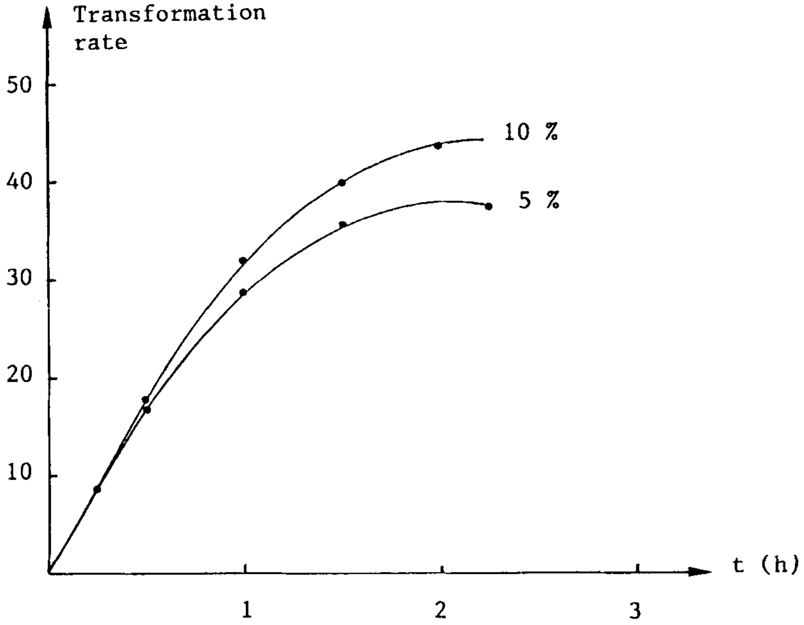


FIGURE 5. Transformation rates of phenol versus time for 5 % and 10 % of the catalyst A

## Influence of the quantity of catalyst

This study was carried out by using the catalyst A dispersed in the solid phenol. Figure 5, which gives the rate of transformation of solid phenol for both quantities of the catalyst used, 5 % and 10 % of the weight of the phenol, also shows that the reactivity in the solid state is not notably modified by the quantity of the catalyst used.

## In the liquid state and in solution

Alkylation reactions carried out at 70°C in the presence of catalyst A and B show that, under these conditions, the reactivity varies depending upon the nature of the catalyst. In the liquid state, at 45°C and 70°C, the proportion of catalyst considerably modifies the reactivity.

As regards to selectivity, see Figures 6 and 7. Whatever the catalyst used, C-alkylation is predominant at 70°C whereas O-alkylation becomes very great at 45°C. In the same way we have observed the almost exclusive formation of tert-butylphenylether at 30°C in solution in the cyclohexane.

## Comparison of the results - solid state and liquid state

In figure 8 we have outlined the reactivities of a type A catalyst at a 5 % proportion, in the liquid state, in the solid state and in solution for different reaction times. It is to be noted that in the liquid state the reactivity decreases considerably when one passes from 70°C to 45°C. In the case of the solid state at 30°C the reactivity is very similar to that of the liquid state at 70°C and, in any case, much higher than that obtained from the liquid state at 45°C. In solution under the temperature

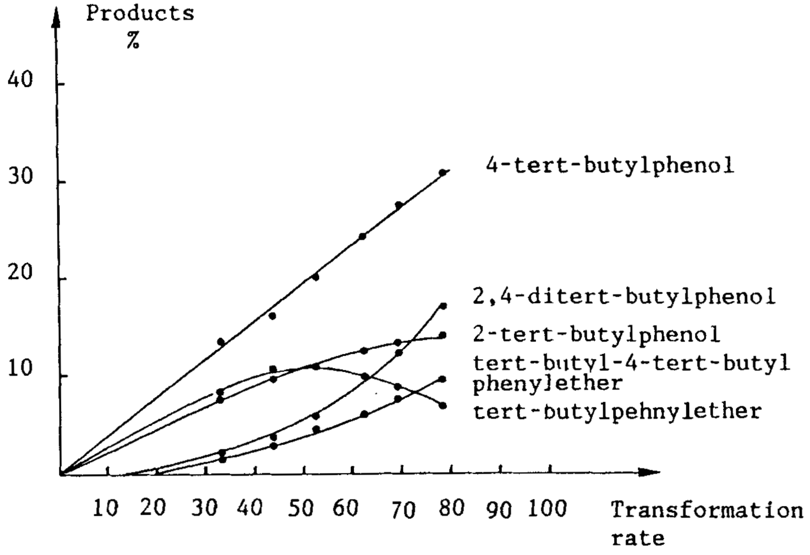


FIGURE 6. Proportion of obtained products versus transformation rate (catalyst A : 5 % ; reaction temperature 70°C)

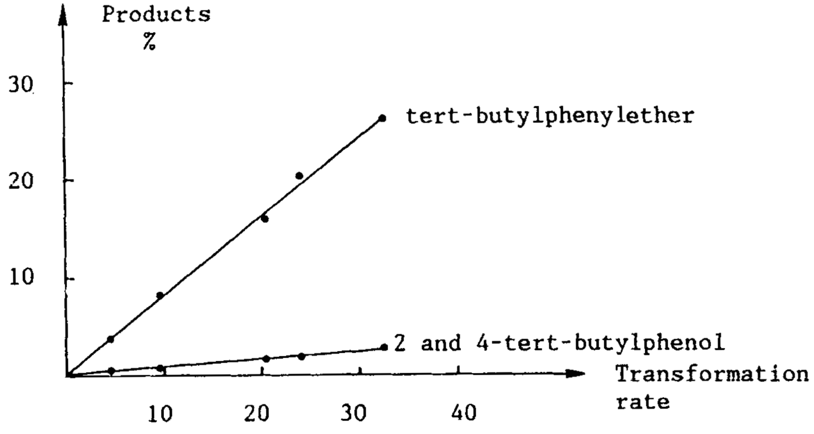


FIGURE 7. Proportion of obtained products versus transformation rate (catalyst A : 5 % ; réaction temperature 45°C)

conditions of the solid state, we have observed that reactivity is low. Thus the solid state appears to be very reactive. This difference of reactivity which has been observed between, on the one hand, the solid state and on the other hand, the liquid state and the solution allows us to presume that we are dealing with an organic solid state reaction[11].

The selectivities, compared at constant rate of transformation, show that in the solid state the O-alkylation is preponderant. Thus, for a transformation rate of 20 %, the ratio O-alkylation/C-alkylation is

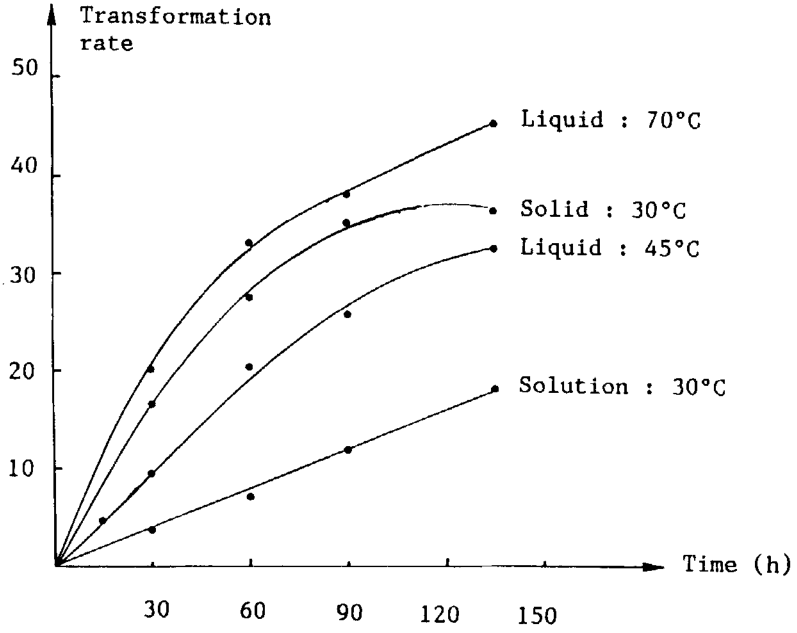


FIGURE 8. Comparison of the reactivities for solid state, liquid state and solution.

7 whereas in the liquid state at 70°C, this ratio is equal to 0.43. It should be noted that the value of the ratio O alk./C alk. for the solid state is close to that obtained in the liquid state at 45°C and in solution at 30°C. This result confirms the rôle of the temperature in the alkylation reactions of phenols. When the temperature drops, the conditions of alkylation are milder and it is phenylethers which are essentially formed[12].

## Mechanistic Aspect

The reaction which took place at 30°C between the gas isobutene and the solid phenol in the presence of a solid catalyst was a heterogeneous reaction composed of 3 phases. The high reactivities which were observed from the beginning of the reaction (Figure 8) indicated that we were indeed experiencing a solid state reaction. In fact, if we assume that the reaction took place in a fluid phase, we should have observed a slow reaction at the beginning, probably slower than that of the liquid state at 45°C, followed by a progressive increase in rate as the fluid phase developed.

To explain the high rates of transformation, we can imagine a similar mechanism to that proposed for the hydrogenation reactions in the solid phase[13]. The isobutene in contact with the solid catalyst produces activated isobutene which migrates into the midst of the solid catalyst and the solid organic reagent.

## CONCLUSIONS

In this work we have shown that it was possible to alkylate solid aromatic substances by alkenes in the presence of solid catalysts. Two phosphoric acid based solid catalysts were prepared. The different reactivity of these two catalysts pointed to the role of water in this type of reaction and confirmed the results previously obtained[14]. Taking into account the proportion of catalyst used and the dispersion of the solid catalysts in the solid phenol, in order to explain the high rates of transformation obtained it is necessary to envisage a transfer of active entities from the solid catalyst to the organic reagent. This corresponds to the spillover effect taken into consideration in the case of hydrogenation of organic solids[15].

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