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THE FIRST APPLICATION OF ANION-CATALYZED PHASE-TRANSFER CATALYSIS TO FRIEDEL-CRAFTS ALKYLATION

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Friedel-Crafts alkylation proceeded by catalysis of tetrakis[3,5-di(*F*-methyl)phenyl]borate (TFPB) in a dichloromethane-aqueous sulfuric acid two-phase system. Kinetic evidence indicated that oxonium-TFPB ion-pair in the organic phase was operative as a catalyst.

A successful application of tetrakis[3,5-di(*F*-methyl)phenyl]borate (TFPB) to anion-catalyzed phase-transfer catalysis (PTC) in the reaction of diazonium ion1) then prompted us to examine the efficacy of PTC system in the Friedel-Crafts alkylation, which could be considered to proceed through the intermediacy of ion-pairing of a carbocation and the anionic catalyst.

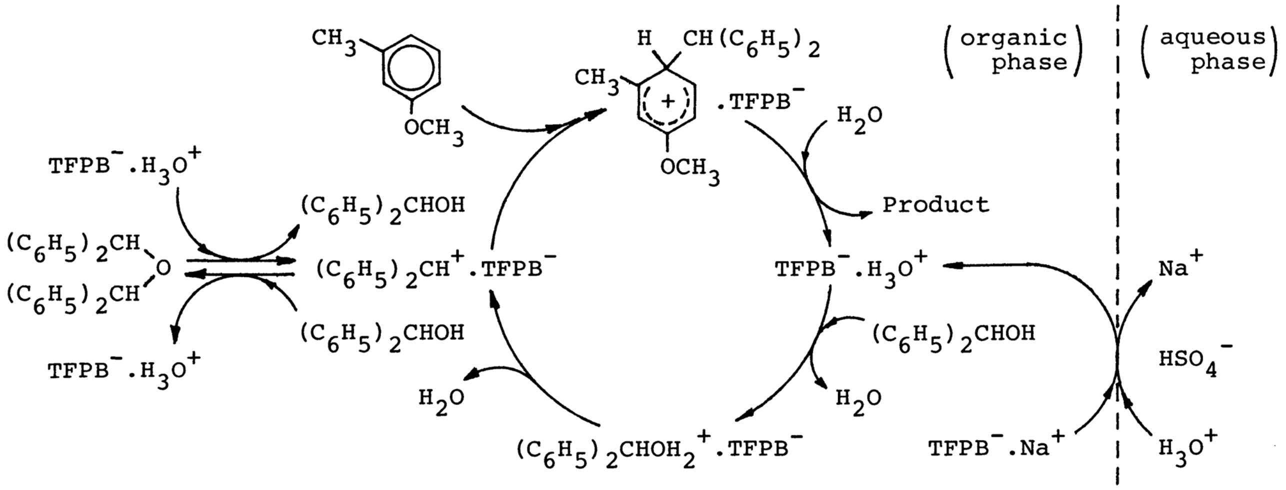
In the present model reaction, the carbocations were derived *in situ* from a range of arylcarbinols such as triphenylmethanol(1a), diphenylmethanol(1b), *p*-methoxybenzyl alcohol(1c), and α-methylbenzyl alcohol(1d) in a two-phase system of dichloromethane and an equal volume of 0.5 mole.l^{-1} aqueous sulfuric acid. A mixture of a carbinol and two- or three times molar quantity of a substrate such as *m*-dimethoxybenzene(2a), *m*-methylanisol(2b), or *o*-cresol(2c) in the two-phase system was stirred well for one day at room temperature in the presence of approximately one mole % of sodium TFPB. The alkylation occurred at the position *para* to the hydroxyl- or methoxyl group, to give a monosubstituted product(3). The alkylation of (2a) with (1a), (2a) with (1b), and (2b) with (1b) gave the respective (3) in the yields of 31, 86, and 66 %, sometimes accompanied by the formation of a considerable amount of the corresponding dicarbinyl ether. For prolonged reaction period, or with an increased amount of the carbinol, *ortho*,*para*-disubstituted product(4) was obtained in addition to the monosubstituted one(3); for example, the reaction of (1c) and (2c) gave the corresponding (3) and (4) with the yields of 78 and 18 %, respectively, and from (1d) and (2c) in a similar manner the corresponding (3) and (4) were obtained in 77 and 23 % yields. No such reactions proceeded without sodium TFPB under the present conditions.

Kinetics of the reaction of (1b) (0.13 mole.l^{-1}) and (2b) (0.024 mole.l^{-1}) under pseudo-first-order conditions was followed at 25°C in the presence of sodium TFPB (1.1×10^{-4} -- 3.3×10^{-5} mole.l^{-1}) by high-performance liquid chromatography, where thermodynamic activities of sodium- (0.10 mole.l^{-1}), oxonium- (1.00 mole.l^{-1}), and sulfate ions (0.55 mole.l^{-1}) in an aqueous phase were considered constant. In a similar manner to that in ordinary PTC systems, apparent first-order kinetic plots covering more than one half-life of the substrate were obtained with a correlation coefficient(γ) greater than 0.98. The pseudo-first-order rate constant(k_1'), thus obtained was directly proportional with γ of 0.99 to the catalyst concentration in the organic phase, and the gradient of correlation line gave the overall second-order rate constant(k_2) of 4.05 mole^{-1}.l.sec^{-1} to the present reaction system. When the kinetics of the same reaction was followed in a wet dichloromethane solution which was equilibrated in advance with 0.5 mole.l^{-1} aqueous sulfuric acid in the presence of 5.0×10^{-5} mole.l^{-1} of sodium TFPB, otherwise under the identical conditions, an apparent first-order kinetic plot covering more than one half-life of the substrate(2b) was obtained with γ of 0.99. The k_2 calculated from the k_1' and the catalyst concentration was 3.8 mole^{-1}.l.sec^{-1}, which, being comparable to the value in the two-phase system, would indicate that the generation of carbocation should take place predominantly in the organic phase.

Although the formation of dicarbinyl ether seemed to precede the alkylation, the resulting ether could be reversely cleaved to re-generate the carbinyl cation under the present reaction conditions; for example, the bis(diphenylmethyl) ether and (2b) afforded the corresponding alkylated product(3) in a wet dichloromethane solution in the presence of oxonium-TFPB ion-pair, while the reaction between (1b) and (2b) catalyzed by dodecylbenzenesulfonic acid in place of RFPB, afforded only bis(diphenylmethyl) ether and no alkylated products at all.

The whole cycle of catalysis can be summarized in the following Scheme, where the oxonium-TFPB ion-pair, which is transfered into the organic phase once at the beginning of the reaction, is re-generated after one cycle, then to catalyze the next cycle. This scheme convinces us that the reaction rate was affected to much less extent by stirring speed, even slower than 300 rpm being efficient enough.

Further kinetic studies are under way in this laboratory.



Reference

1) H. Kobayashi, T. Sonoda, H. Iwamoto, and M. Yoshimura, *Chem. Lett.*, 1981, 579.

2) TFPB salt is highly lipophilic, and its sodium salt is practically insoluble in water, but readily dissolved in dichloromethane.[1]

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