High Pressure Reactions, I
Evidence for Two Concurrent Mechanisms in Lewis-Acid Catalyzed Alkylation of Aromatics with Olefins

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Friedel-Crafts Alkylation, Aromatics, Olefins, High Pressure Kinetics, Concurrent Mechanisms

A kinetic study was made of the primary step of the alkylation of benzene with propylene and ferric chloride as catalyst under homogeneous reaction conditions at several pressures up to 2 kbar. Initial reaction rate of cumene formation shows a minimum in the medium pressure range, thus indicating that product formation occurs *via* two different reaction paths with opposite pressure dependence.

In spite of the immense quantity of literature dealing with reactions of Friedel-Crafts type (for survey see [1]) the number of papers concerning kinetic investigations of such systems, on the other hand, is very small. The mechanism which was generally accepted for a long time involves formation of carbocations, which rapidly attack the aromatic nucleus by electrophilic substitution[2]. In contrary according to the investigations of H. C. Brown and coworkers[3], the reaction of benzylhalides with aromatic compounds is third order, first order in aromatic component, first order in catalyst and first order in the alkylating agent, thus indicating a displacement mechanism. But there is a number of observations which cannot be satisfactorily explained by a pure displacement mechanism, especially when alkylation is carried out with higher *n*-alkylhalides or olefins. Conversion is almost always accompanied by rearrangements of the alkylating agent. For example 40–60% formation of isopropylbenzene is reported in the alkylation of benzene with *n*-propylhalides[4]. But since isomerization also takes place in the absence of the aromatic component, it is difficult to get quantitative information about the extent of possible contribution of intermediately formed carbocations to the alkylation process. Uncertainty also exists about the rate determining step, – formation of π-complex or of σ-complex or even another step of these consecutive reactions. In the same way orientations in Friedel-Crafts alkylations frequently are considered to be anomalous; temperature, solvent, nature and amount of catalyst seem to have a large effect on the orientation of the products formed.

In order to get an answer to some of these questions we made a kinetic study of the primary step of the alkylation of benzene with propylene and ferric chloride as a mild catalyst under homogeneous reaction conditions in nitrobenzene solution. Since the application of pressure is a sensitive method for the investigation of reactions involving formation or disappearence of polar species in the rate determining step[5], we extended our experiments to pressures up to 2 kbar. The experimental technique of this procedure is described in detail elsewhere[6]. The analyses were carried out by gas-liquid chromatography on a Perkin-Elmer model 900 vapor fractometer, combined with an electronic integrator SIP 1.

Kinetic results, obtained by the method of initial reaction rate, which is the only suitable kinetic method in this case in order not to fail with unwanted side reactions, revealed that the reaction is first order in ferric chloride. The variation of propylene concentration over a wide range showed within experimental error no dependence of reaction rate from the olefin; propylene reacts zeroth order. The effective alkylating agent at low pressure is isopropylchloride, formed in a fast preceding reaction by conversion with the needed cocatalyst hydrogenchloride. The concentration of cocatalyst contributes to the rate equation with first order and we could not find a measurable difference while varying the concentration of hydrogenchloride or that of isopropylchloride in the equivalent manner. Detectable small conversions under exclusion of cocatalyst could be traced back quantitatively either to small amounts of humidity introduced to reaction mixture by the solvent or reactants, respectively, or to the decomposition of catalyst employed.

The determination of order with regard to benzene at normal pressure gave an indication that the reaction is still more complex (Fig. 1). Although the values show clearly a dependency of reaction rate from benzene concentration, the slope of the curve does not confirm an exact first order. To conclude from these results only to a broken order of benzene seems to be problematic, since an experimental error of ±5 to ±3% has to be considered, according to the initial concentration. But our kinetic experiments at high pressure brought a confirmation of these findings, shown in Fig. 2. Accordingly, initial reaction rate is retarded with increasing pressure, attains a minimum and is accelerated by further compression. As theoretically pointed out by Kohnstam[7] such a pressure dependence may be indicative that product formation occurs *via* two different reaction paths which are opposite in pressure dependence. The experimentally measured reaction rate represents the sum of the rates of two

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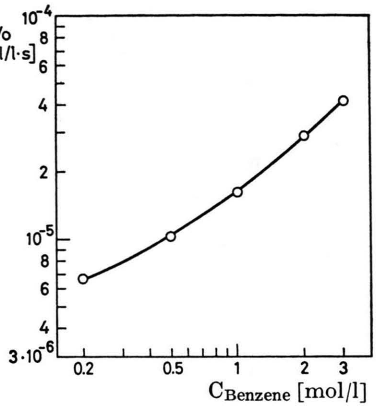

Fig. 1. Influence of benzene concentration on initial alkylation rate.

Reaction conditions:
Temperature: 50 °C,
$c_{propene}$: 1,6 mole/l,
$c_{cat.} = c_{cocat.}$: $6{,}2 \cdot 10^{-3}$ mole/l.

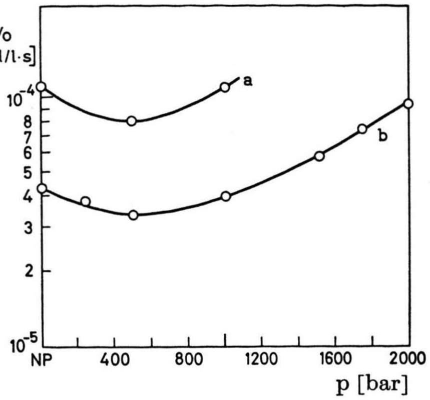

Fig. 2. Influence of pressure on initial reaction rate.

Reaction conditions:
Temperature: 50 °C,
$c_{propene}$: 1,6 mole/l,
$c_{benzene}$: 3,05 mole/l,
$c_{cat.} = c_{cocat.}$: $16{,}3 \cdot 10^{-3}$ mole/l (a),
$6{,}2 \cdot 10^{-3}$ mole/l (b).

concurrent processes. While process 1 is predominant at low pressure, its influence is weakened when pressure is raised and process 2 becomes predominant at high pressures.

These results confirm the suggestion outlined by H. C. **Brown** already in 1953[3] that principally two different mechanisms should be considered in alkylation reactions. We believe, high pressure kinetics is a suitable tool to get quantitative information about the single reactions contributing to the overall alkylation at normal pressure.

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