[CONTRIBUTION FROM THE DIVISION OF APPLIED CHEMISTRY, NATIONAL RESEARCH COUNCIL]

Co-catalysis in Friedel–Crafts Reactions. I. Boron Fluoride–Water

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RECEIVED AUGUST 2, 1956

The rate of *cis–trans* isomerization of butene-2 has been studied in ethylene chloride solution with boron fluoride–water mixtures as catalyst. The rate is markedly dependent upon water concentration and reaches a sharp maximum at a $BF_3 \cdot H_2O$ ratio of approximately 2:1. At higher water concentrations the rate falls off very sharply and complete poisoning eventually results, presumably due to the formation of $BF_3 \cdot 2H_2O$.

The polymerization of isobutene by boron fluoride requires the presence of water, acetic acid or some other proton-donating substance as a co-catalyst.[1] Although rigorously demonstrated only for the isobutene reaction, this co-catalysis is probably present in a great many Friedel–Crafts reactions and accounts for the difficulty in obtaining satisfactory kinetics for them. To explain the re-results, Evans and Polanyi[2] suggested that the true catalyst in the BF_3–H_2O system is the conjugate acid HBF_3OH, which initiates polymerization through proton transfer and formation of a carbonium ion intermediate, *viz.*

$$H_2O + BF_3 \longrightarrow HBF_3OH \tag{1}$$

$$HBF_3OH + R_2C{=}CH_2 \longrightarrow R_2\overset{+}{C}{-}CH_3 \dots BF_3OH^- \tag{2}$$

$$R_2\overset{+}{C}{-}CH_3 + R_2C{=}CH_2 \longrightarrow R_2\overset{+}{C}{-}CH_2{-}R_2C{-}CH_3, \text{ etc.} \tag{3}$$

This view is generally accepted today but with reservations as to the actual nature of the BF_3–H_2O complex since there seems to be no direct evidence for the compound HBF_3OH.[3]

Information about the co-catalysis has come largely from polymerization studies. However if the above mechanism is sound, it should be possible to examine reactions 1 and 2 alone by measuring the rate of *cis–trans* isomerization for a non-polymerizing olefin and thus avoid the complications resulting from polymer formation. The isomerization should presumably proceed through the transitory addition of a proton and thus be equivalent to a reversible reaction 2.

Some qualitative work of this kind has been attempted with stilbene as the monomer,[4] but the results have been contradictory and stilbene in any event is not satisfactory because of possible interference from the aromatic nucleus. Butene-2 would seem to be the logical reactant because of its simplicity, resistance to polymerization, ease of handling in a vacuum system, and ready availability in the *cis* and *trans* forms. Surprisingly, however, it has been reported[5] that butene-2 is polymerized but not isomerized by BF_3–H_2O, a result which would suggest that the initiation step is very efficient, *i.e.*, that reaction 2 is not reversible. This seems rather unlikely, especially since an induction period was observed. The experiments were carried out with very large concentrations of boron fluoride and without close control over the water concentration so it seemed worthwhile to attempt a more rigorous examination of the reaction.

In preliminary experiments, dioxane, benzene, cyclohexane and ethylene chloride were examined as possible solvents, with and without added water. Isomerization was observed only in benzene and ethylene chloride, but the former is unsatisfactory for a variety of reasons so ethylene chloride was selected for further studies. Dioxane probably inhibits reaction by complexing with the boron fluoride, but cyclohexane will have to be re-examined in the light of the results in this paper.

Experimental

Materials.—Boron fluoride was dried by repeated evaporation from sodium mirrors and was stored in a gas bulb on the vacuum system.

Some difficulty was experienced in adequately drying the butenes, but satisfactory results were eventually obtained by allowing the liquid to evaporate about 15 times, under its own pressure, through six feet of half-inch glass tubing coated with a sodium mirror. The mirror was warmed from time to time to give it a fresh surface and the drying, for best results, was carried out over several days. This treatment produced no appreciable (<0.3%) isomerization of *trans*-butene.

Ethylene chloride was washed several times with concentrated sulfuric acid, then with water and was dried with sodium carbonate followed by phosphorus pentoxide. The product was allowed to stand for some time over, and was then distilled from, aluminum chloride. It was treated again with sodium carbonate and phosphorus pentoxide, then carefully fractionated before being degassed and stored over phosphorus pentoxide on the vacuum system. In solvent thus prepared, phosphorus pentoxide remains dry and powdery for at least eight months.

Apparatus and Method.—All materials were stored, handled, reacted and analyzed in an all-glass vacuum system. Mercury pumps and manometers were used without removal of mercury vapor from the reaction zone. Stopcocks were lubricated with Apiezon N grease and cleaned when necessary with cyclohexane. Degassing and drying of the apparatus was accomplished by pumping, flaming and sparking with the leak tester; by prolonged treatment the system could be degassed to the point where it would hold a "sticking" vacuum for some hours, but for most runs an adequate vacuum was obtained after a day or two.

The reaction flask, of about 100 cc. capacity and containing a small magnetic stirrer, was so arranged that small (*ca.* 1 cc.) liquid samples could be siphoned out into an evacuated receiver on the analytical system. The number of samples withdrawn from any one run was limited to about five because the grease on the siphon stopcock was removed by the solvent.

Boron fluoride and water were measured out in small gas bulbs with attached mercury manometers and condensed into the reaction flask at liquid nitrogen temperature. Solvent (35 cc.) was then distilled in, followed by *trans*-

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[1] A. G. Evans and G. W. Meadows, *Trans. Faraday Soc.*, **46**, 327 (1950).

[2] A. G. Evans and J. Polanyi, *J. Chem. Soc.*, 252 (1947).

[3] P. H. Plesch, "Cationic Polymerization," Heffer, Cambridge, 1953, p. 28.

[4] C. C. Price and M. Meister, THIS JOURNAL, **61**, 1595 (1939); D. C. Downing and G. F. Wright, *ibid.*, **68**, 141 (1946); C. C. Price and G. Berti, *ibid.*, **76**, 1219 (1954); D. S. Brackman and P. H. Plesch, *J. Chem. Soc.*, 1289 (1953).

[5] R. L. Meier, *ibid.*, 3656 (1950).

butene-2. Water at 25.0° was circulated around the flask which was stirred vigorously until liquefaction of the reagents was complete.

Samples of the mixture were run out at intervals onto a drop of diethanolamine to stop the reaction. The butenes were distilled out of the sample through a small column packed with helices and fitted with a low temperature cold finger to provide reflux. After one or two more distillations, the butenes were condensed into the gas cell of a Beckman IR-2 infrared spectrometer for analysis. Care had to be taken at all times to prevent fractionation of the butenes during evaporations at low pressure.

cis–trans mixtures of known composition gave an almost linear relationship between % *cis*-butene and optical density when measured at 14.8 μ and 100 mm. gas pressure. The accuracy was about ±0.2% *cis*-butene with the pure gases but fell off to about ±0.4% for the analysis of solution samples. The equilibrium concentration of *cis*-butene was found to be about 26% and the equilibrium mixture contained in addition to the *cis–trans* isomers about 8% of 1-butene as part of a ternary system. The 1-butene has been ignored throughout this work. Mass spectrometric examination of the gases obtained from the reaction mixtures showed only butenes contaminated by traces of solvent.

The reactions were too rapid for the direct estimation of initial rates. The plot of log $(x_0 - x)/t$ for a first-order equilibrium process, held fairly well up to about 10% *cis* (less than one half-life) after which it fell off; it was used to estimate rates where three or four points could be obtained in the linear range. For the faster runs it was necessary to estimate the rates by comparing the times required to reach a given conversion.

Results

When experiments showed that water, in concentrations somewhat greater than that of boron fluoride, completely poisoned the isomerization and that addition of triphenylmethyl chloride and of β-chloropropionic acid also resulted in poisoning, it seemed that co-catalysis was not necessary for this reaction. However, subsequent runs under supposedly anhydrous conditions failed to give reproducible results so much smaller quantities of water were added and were found to produce acceleration. As a result, a completely new vacuum system was built and thoroughly evacuated before attempting further experiments. The curves in Fig. 1 show the results of the first six runs in the new apparatus. The rates decreased steadily, presumably because incidental water was being worked out of the system. Three days were spent degassing before run 5 and nearly two weeks before run 6. In addition, the butene was again thoroughly treated with sodium before run 6. The nearly identical rates for runs 5 and 6 indicated that the practical limit of drying had been reached at this point.

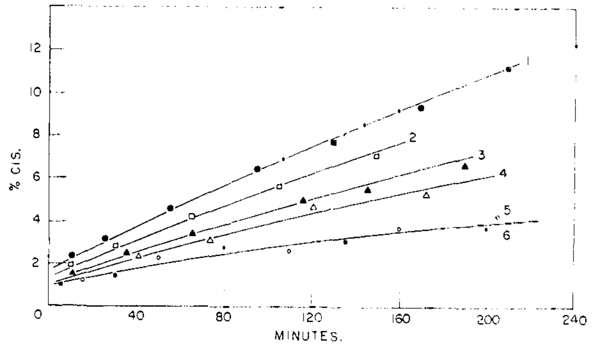

Fig. 1.

If water was the cause of the slow isomerization in runs 5 and 6 then it most probably entered with the solvent which was identical for both runs. The amount of such water can be estimated roughly from the curves of Fig. 2 and comes to about 1 mg./l. (0.5 p.p.m.) which, though not a great deal, seems rather more than would be expected in a solvent stored over dry phosphorus pentoxide for at least six months. It is possible therefore that there is a slow reaction without co-catalysis or with solvent co-catalysis or, alternatively, that the solvent may contain a trace of some other co-catalyst not removed by the purification process.

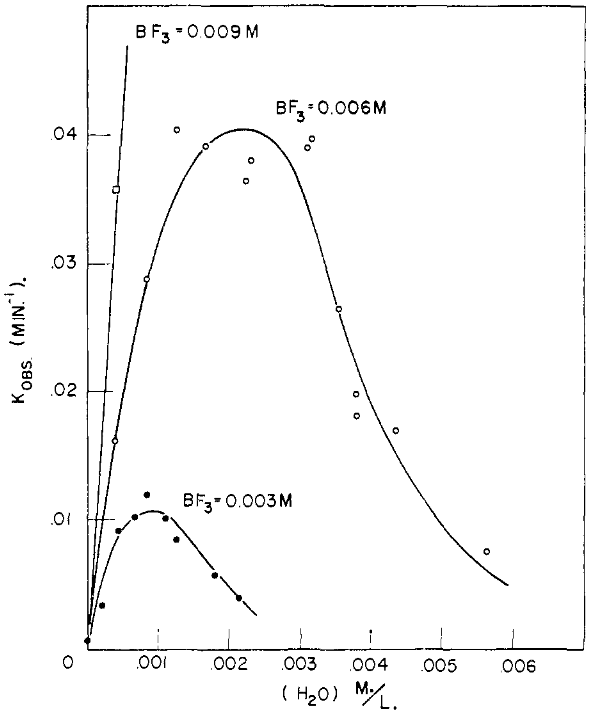

Fig. 2.

The intercept of the curves at about 1.5% *cis*-butene could be due to a short-lived, very rapid reaction but is more probably due to some experimental error. It was not observed with either known mixtures or with completely poisoned reactions. Some error undoubtedly occurs due to reaction during the thawing of the reagents, but it is unlikely that the temporary high concentrations of butene and boron fluoride could produce an error of this magnitude.

The curves in Fig. 2 show the dependence of the rate of isomerization upon the concentrations of catalyst and co-catalyst. The initial concentration of *trans*-butene was 1.0 *M;* the concentrations of boron fluoride are expressed as total BF_3 added/volume of solvent, without allowance for the considerable amount of catalyst which must be in the vapor phase, particularly at low water concentration.

The reaction is probably first order with respect to butene, but this point was not definitely established because the present apparatus did not permit sufficient variation in the butene pressure. A two- to threefold change, however, did not appreciably alter the observed rate constant.

No appreciable polymerization of the butene was observed and the amount of gas distilled from the samples remained fairly constant throughout the runs. Solution appeared to be complete in all cases.

Discussion

It is difficult to assess the accuracy of the data in Fig. 2. Considerable error in the water concentration is possible, especially at the lower end of the scale due to absorption of the vapor by walls, stopcock grease, etc., during the transfer from the measuring bulb to the reactor. The fact that the results are reasonably consistent and reproducible suggests that the error from this source is not as great as might be expected, but nevertheless may be important at low water concentrations. The observed rate constants were obtained fairly easily up to a value of about 0.01 min.$^{-1}$ but their reliability decreased steadily above that point. The highest rates are essentially estimates as is evident from their scatter.

In spite of their semi-quantitative nature, the results provide some useful information. The sharp peak in the rate with respect to water concentration doubtless accounts for much of the confusion in the literature reports of work in this field, but it must be remembered that the present results are quite possibly characteristic of a limited number of solvents. Furthermore, because of the experimental difficulties involved, and the ease with which the reactions can be poisoned or catalyzed, any results must be regarded with considerable caution until confirmed by independent investigations.

The data shed little light on the detailed mechanism of the catalysis. If toxicity of water at higher concentrations is due to the formation of the dihydrate, $BF_3 \cdot 2H_2O$, which is inactive in catalyzing polymerization, then the rate of isomerization is presumably governed by the equilibria

$$BF_3 + H_2O \xrightleftharpoons{K_1} HBF_3OH$$

$$HBF_3OH + H_2O \xrightleftharpoons{K_2} BF_3 \cdot 2H_2O$$

K_2 is probably large, since $BF_3 \cdot 2H_2O$ is a stable compound, which accounts for the rapid poisoning of the reaction with increasing water concentration. At low water concentrations the rates seem roughly proportional to the total concentrations of water and of boron fluoride, but because of the relationship $(HBF_3OH) = K_1(BF_3)(H_2O)$ this cannot be taken as evidence for catalysis by the conjugate acid; a termolecular process involving free water and catalyst is conceivable. More accurate kinetic data together with a knowledge of the constants K_1 and K_2 might help to distinguish between these possibilities but much would depend on the actual values of K_1 and K_2. An effort is being made to obtain such data.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE AGRICULTURAL AND MECHANICAL COLLEGE OF TEXAS AND THE RESEARCH AND DEVELOPMENT LABORATORIES OF THE AMERICAN OIL CO.]

A Study of the Reaction of Hydrocarbons with Phosphorus Trichloride and Oxygen[1]

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RECEIVED JUNE 28, 1956

A study was made of the factors which influence the yield of alkylphosphonyl dichloride when reaction takes place between a hydrocarbon, phosphorus trichloride and oxygen. Changing the molar ratio of phosphorus trichloride to hydrocarbon changes the yield of alkylphosphonyl dichloride within limits but reaction temperature has virtually no influence. The reaction is very sensitive to impurities. Four new cycloparaffins were employed in the reaction. Nitrocyclohexane, cyclohexene, isopropylbenzene and acetyl chloride failed to react.

The reaction between hydrocarbons, phosphorus trichloride and oxygen, to produce alkylphosphonyl dichlorides, was first described by Clayton and Jensen[4] in 1948. Since that time, they and other workers[4-14] have extended this reaction. However, the reported yields of the same products have varied widely, experimental conditions have usually been described inadequately and the effects of changes in experimental conditions have not been made clear. We have attempted to make a more thorough study of this reaction.

There is relatively little information in the literature relating simply to the oxidation of phosphorus trichloride to phosphorus oxychloride. Some of this is in disagreement. Certain references[15-19]

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(3) American Oil Company.

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