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# Cocatalysis in Friedel–Crafts Reactions. II. Boron Fluoride–Water

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Vapor pressure measurements on the system ethylene dichloride–water–boron fluoride have led to a value for the equilibrium constant $K = (BF_3)(BF_3{\cdot}2H_2O)/(BF_3{\cdot}H_2O)^2$. From this value it appears that the rate of isomerization of 2-butene by boron fluoride–water mixtures in ethylene dichloride is governed by the expression $dI/dt = k(BF_3)(BF_3{\cdot}H_2O)(\text{butene})$.

A previous paper[1] reported the results of some measurements of the rate of isomerization of *trans*-2-butene by boron fluoride–water mixtures in the solvent ethylene dichloride. In that work, it was found that at constant total boron fluoride concentration, the rate of isomerization passed through a maximum with increasing water concentration. It was assumed that this maximum rate corresponded to a maximum in the concentration of the acid $HBF_3OH$ which, according to the theory of Evans and Polanyi,[2] is the true catalyst in the system. The concentration of this catalyst would be controlled by the equilibria $(HBF_3OH/BF_3)\cdot(H_2O) = K_1$ and $(H_3O^+{\cdot}BF_3OH^-)/(HBF_3OH)\cdot(H_2O) = K_2$, so an exact interpretation of the kinetics obviously requires some knowledge of the constants $K_1$ and $K_2$. The present paper reports an effort to obtain such information from an examination of the vapor pressure of boron fluoride over solutions of water in ethylene dichloride.

## Experimental

The methods for preparing, storing and handling materials were generally similar to those previously reported.

Vapor pressure measurements were made in a magnetically stirred, round bottom flask (63 ml.) attached through a stopcock to the vacuum line and through a side arm to a constant volume manometer. The flask was maintained at constant temperature by circulating water from a thermostat and was calibrated by condensing into it known volumes of boron fluoride. It was thoroughly degassed between runs and was cut off the system occasionally to remove condensed mercury, stopcock grease, etc.

For the measurements, 25 ml. of ethylene dichloride was condensed into the flask, the vapor pressure checked and water then added. Water was measured as the vapor in a calibrated bulb; the pressure was kept well below the saturation vapor pressure to minimize errors due to adsorption on the walls[3] and was measured by means of a manometer filled with silicone oil (General Electric LTNV-40).

Aliquots of boron fluoride were then condensed into the mixture and the pressure determined after each addition. The mixtures were stirred vigorously and were considered to be in equilibrium when the pressure variation in fifteen minutes was less than 0.3 mm.

## Results

In Fig. 1 the vapor pressure of boron fluoride is plotted against the total concentration of boron fluoride taken up by the solvent. It is clear that in the presence of water a rather small molar excess of boron fluoride is sufficient to convert the water completely to a 1:1 complex; furthermore with excess water there appears to be no boron fluoride vapor pressure at all. There is, therefore, as might be expected, a very strong association between these two compounds and probably very little free water in solution.

If one can assume that the free water concentration is in fact quite small compared to $BF_3{\cdot}H_2O$ and $BF_3{\cdot}2H_2O$, it becomes possible from the data to estimate the equilibrium constant

$$\frac{(BF_3)(BF_3{\cdot}2H_2O)}{(BF_3{\cdot}H_2O)^2} = K_2/K_1 = K_3$$

and the results of these calculations for the system at 20° are shown in Table I.

TABLE I

CALCULATION OF THE EQUILIBRIUM CONSTANT

| System no. | $H_2O$ in soln. $\times 10^3$ (total), g. mole l.$^{-1}$ | $BF_3$ in soln. $\times 10^3$ (total), g. mole l.$^{-1}$ | Free $(BF_3)$ in soln., $\times 10^3$ g. mole l.$^{-1}$ | $(BF_3{\cdot}2H_2O)$ in soln. $\times 10^3$, g. mole l.$^{-1}$ | $(BF_3{\cdot}H_2O)$ in soln. $\times 10^3$, g. mole l.$^{-1}$ | $K_3 \times 10^3$ |
|---|---|---|---|---|---|---|
| II | 9.125 | 9.005 | 0.554 | 0.674 | 7.777 | 6.19 |
| III | 19.33 | 18.09 | 1.089 | 2.33 | 14.67 | 11.80 |
| IV | 31.48 | 28.97 | 1.334 | 3.84 | 23.80 | 9.04 |
| IV | 31.48 | 34.35 | 4.538 | 1.67 | 28.14 | 9.57 |
| V | 39.07 | 24.10 | 0.0565 | 15.02 | 9.02 | 9.88 |
| V | 39.07 | 29.75 | 0.2959 | 9.616 | 19.83 | 7.23 |
| V | 39.07 | 34.65 | 1.183 | 5.603 | 27.86 | 8.54 |
| V | 39.07 | 37.98 | 2.518 | 3.608 | 31.85 | 8.96 |
| V | 39.07 | 40.64 | 4.350 | 2.780 | 33.51 | 10.77 |
| V | 39.07 | 43.53 | 6.295 | 1.835 | 35.40 | 9.22 |
| V | 39.07 | 46.15 | 8.403 | 1.323 | 36.42 | 8.41 |
| | | | | | Average | 9.0 |

The constancy of $K_3$ is about as good as can be expected from measurements of this type and seems to justify the assumption of little free water in the system. At 25° the corresponding value for $K_3$ is $2.0 \times 10^{-3}$.

## Discussion

From the vapor pressure data, $K_3$, and the total concentrations of water and boron fluoride, the concentrations of the mono and dihydrates can be calculated. When one applies the results of such calculations to the earlier kinetic data it becomes immediately apparent that little correlation exists between rate and the concentration of monohydrate. Very much better results are obtained, as is shown in Fig. 2, if the variation of the product $(BF_3)(BF_3{\cdot}H_2O)$ is compared with the rates. There is a slight displacement of the kinetic data toward low water concentrations due most probably to the fact that errors due to the adsorption of water on the walls of the measuring vessel were proportionately greater with the smaller amounts of water used in the kinetic runs. The displacement suggests that the actual water additions were about 0.2 mg. per run greater than the measured vapor pressure and that the error was greatest for the highest water concentration, results which are not incompatible with the data of McHaffie and Lenher[3] for the dispensing of water as vapor.

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[1] A. M. Eastham, THIS JOURNAL, **78**, 6040 (1956).

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

[3] I. R. McHaffie and S. Lenher, *ibid.*, **127**, 1559 (1925).

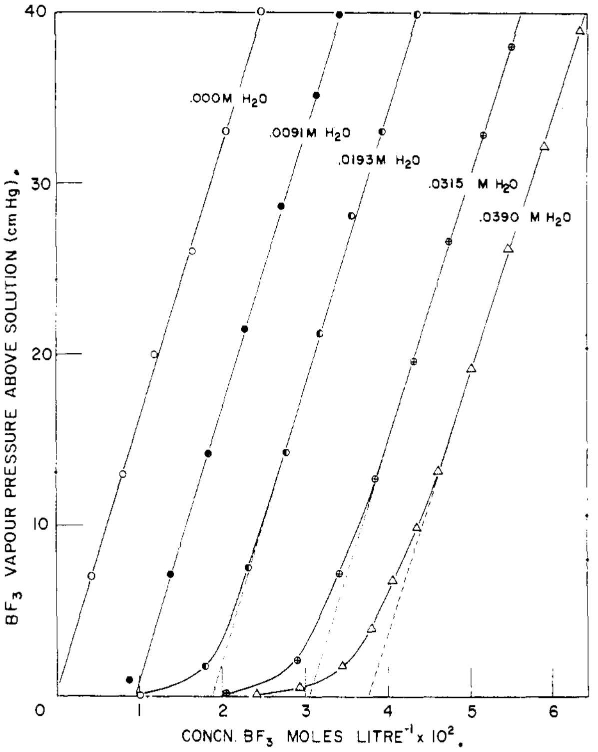

Fig 1.—The vapor pressure of $BF_3$ over solutions of water in ethylene dichloride.

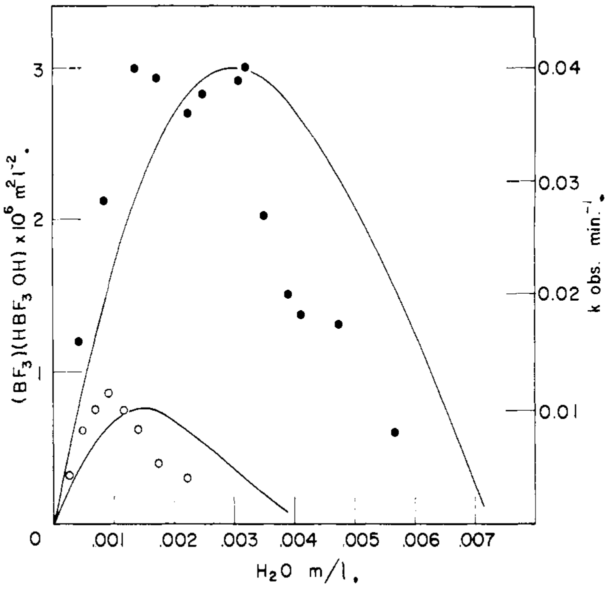

Fig. 2.—Comparison of observed rate of isomerization with calculated (solid lines) values of the product $(BF_3)(HBF_3OH)$: open circles, 0.003 *m;* solid circles, 0.006 *m* total $BF_3$.

There seems good reason therefore to believe that the rate of isomerization of butene is governed by the expression

$$\frac{dI}{dt} = k(BF_3)(BF_3 \cdot H_2O)\ (\textit{trans}\text{-butene})$$

where $k = k_1 + k_{-1} = 1.3 \times 10^4$ mole$^2$ l.$^2$ min.$^{-1}$.

The interpretation of such a rate law is not easy. The apparent dependence on both $BF_3$ and $BF_3 \cdot H_2O$ suggests that a complex $2BF_3 \cdot H_2O$ might be the actual catalyst, but there is no independent evidence for the existence of this complex. Olefins and boron fluoride form weak complexes at low temperatures (Schneider and Lupien, private communication) so a mechanism involving attack of $BF_3 \cdot H_2O$ on the complex butene·$BF_3$ would satisfy the kinetics but seems to have little else to recommend it.

It seems clear from the fact that 1-butene is formed in equilibrium quantities during the isomerization, that reaction must occur through the actual transfer of a proton to the butene to form the ion $CH_3CH_2\text{-}{}^+CH\text{-}CH_3$ or a weak compound $CH_3\text{-}CH_2\text{-}CHX\text{-}CH_3$, and not through any sort of loose complex. However, it is worth noting that, according to recent experiments in this Laboratory, anhydrous perchloric acid in ethylene dichloride solution does not isomerize butene but adds to it to form a fairly stable addition compound. It may be, therefore, that the role of the free boron fluoride in the rate expression is to decompose any stable addition compound between the butene and the boron fluoride monohydrate.

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