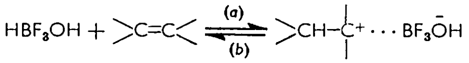
306. *Co-catalysis in Friedel–Crafts Reactions. Part V.*[1] *The Isomerisation of Butenes by Boron Fluoride–Acetic Acid.*

By Joan M. Clayton and A. M. Eastham.

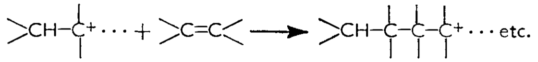
The kinetics of the equilibrium between but-1-ene and *cis*- and *trans*-but-2-ene in ethylene dichloride have been studied by using boron fluoride–acetic acid as catalyst. The results, which show that the rate of isomerisation depends directly on the concentrations of free boron fluoride and of boron fluoride–acetic acid complex but indirectly on the concentration of olefin, have been taken as evidence for a pre-equilibrium between the olefin and the catalyst–co-catalyst complex. Acetic acid is much less effective than water and only slightly more effective than methanol as a co-catalyst.

The polymerisation of olefins by Friedel–Crafts catalysts is generally considered to proceed by a cationic chain mechanism in which the initiation step is a protonation of the olefin to form a carbonium ion. This view is due primarily to Polanyi, Evans, and their co-workers [2] who showed that a Friedel–Crafts catalyst must be associated with a proton-donating molecule (the co-catalyst) in order to produce a polymerisation, and who therefore suggested that the catalyst and co-catalyst together form a strong acid which is responsible for protonation of the olefin.

$$\mathrm{BF_3 + H_2O \rightleftharpoons HBF_3OH} \qquad (1)$$



$$\mathrm{HBF_3OH} + {>}\mathrm{C{=}C}{<} \underset{(b)}{\overset{(a)}{\rightleftharpoons}} {>}\mathrm{CH}-\overset{|}{\underset{|}{\mathrm{C}}}{}^{+}\cdots\mathrm{BF_3\bar{O}H} \qquad (2)$$



$${>}\mathrm{CH}-\overset{|}{\underset{|}{\mathrm{C}}}{}^{+}\cdots + {>}\mathrm{C{=}C}{<} \longrightarrow {>}\mathrm{CH}-\overset{|}{\underset{|}{\mathrm{C}}}-\overset{|}{\underset{|}{\mathrm{C}}}-\overset{|}{\underset{|}{\mathrm{C}}}{}^{+}\cdots\text{etc.} \qquad (3)$$

For some time we have been attempting to study the initiation step in this process by observing the Friedel–Crafts-catalysed isomerisation of *cis*- and *trans*-but-2-ene, on the assumption that the essential difference between isomerisation and polymerisation lies in the relative rates of reactions 2(*b*) and (3). Kinetic studies of the isomerisation in ethylene dichloride, with boron fluoride–methanol as catalyst, have shown [3] that the rate of isomerisation is determined by the concentrations of the catalyst–co-catalyst complex and of the free boron fluoride in solution, but seemingly not by the concentration of olefin. The rate expression under our experimental conditions was, therefore,

$$-\mathrm{d(Isomer\ A)/d}t = \mathrm{d(Isomer\ B)/d}t = k[\mathrm{CH_3{\cdot}OH,BF_3}][\mathrm{BF_3}]$$

The experiments have also shown that the value of the rate constant, *k*, as obtained from initial rate measurements is the same when either the *cis*- or the *trans*-isomer is used as starting material, in spite of the fact that the equilibrium mixture of isomers contains about three times as much *trans*- as *cis*-but-2-ene.

In attempting to account for these results we have consistently been forced to assume the rapid formation, in high yield, of a 1 : 1 : 1 complex between olefin, catalyst, and co-catalyst. The complex cannot be the ether, 2-methoxybutane, since this ether will not function as a co-catalyst. On the whole, the scheme (4, 5) seemed to account for our observations provided that (*a*) complex (I) is formed essentially quantitatively, without loss of olefin configuration; (*b*) complex (II) is formed in low yield; (*c*) configuration is lost in either the formation or the rearrangement of complex (II); (*d*) regeneration of the olefin from complex (II) yields approximately equal amounts of the *cis*- and the *trans*-isomer. The chief weakness in the scheme has been our inability to demonstate the formation of complex (I). This should be simple since, by reducing the concentration of

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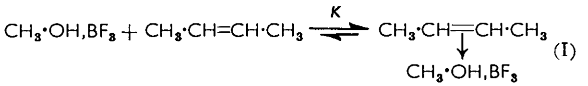
[1] Part IV, Tauber and Eastham, *J. Amer. Chem. Soc.*, 1960, **82**, 4888.

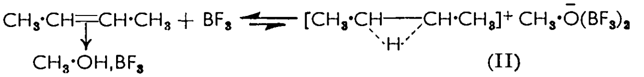
[2] Evans and Polanyi, *J.*, 1947, 242.

[3] Clayton and Eastham, *Canad. J. Chem.*, 1961, **39**, 138.

free boron fluoride, reaction (5) could be eliminated and reaction (4) studied independently. Further, a minimum value can be assigned to K from the kinetic data and used to calculate the concentration range in which measurements of reaction (4) might be made. However, when we attempted to make such measurements by observing the vapour pressure of butene



$$\mathrm{CH_3{\cdot}OH,BF_3 + CH_3{\cdot}CH{=}CH{\cdot}CH_3 \overset{K}{\rightleftharpoons} \underset{\underset{CH_3{\cdot}OH,BF_3}{\downarrow}}{CH_3{\cdot}CH{=}CH{\cdot}CH_3}}\ \mathrm{(I)} \tag{4}$$



$$\mathrm{\underset{\underset{CH_3{\cdot}OH,BF_3}{\downarrow}}{CH_3{\cdot}CH{=}CH{\cdot}CH_3} + BF_3 \rightleftharpoons \underset{(II)}{[CH_3{\cdot}\underset{\cdot H\cdot}{CH{-}{-}CH}{\cdot}CH_3]^+}\ CH_3{\cdot}\bar{O}(BF_3)_2} \tag{5}$$

over solutions of the catalyst–co-catalyst complex, we found that at the high catalyst concentrations employed there was, in fact, some polymerisation of the olefin even in the absence of free boron trifluoride. Attempts to extrapolate the pressures to zero time were not very successful but seemed to indicate that, if any complex was formed, then the value of K must lie close to the minimum value estimated from the kinetic data. Under these conditions the best hope for finding evidence for the pre-equilibrium seemed to lie in extending the kinetic measurements to lower concentrations of reactants to see if increasing dependence on olefin concentration could be observed. This we have now done, using boron fluoride–acetic acid as the catalyst system, and the results provide excellent support for the proposed mechanism.

EXPERIMENTAL AND RESULTS

Ethylene dichloride, the butene isomers, and boron trifluoride were purified and manipulated as described previously.[4]

Acetic acid (C.I.L., 99·8%) was purified twice by fractional crystallisation to yield a small fraction of the original material having m. p. 16·4°. This material was then degassed and stored on the vacuum-system. Measured quantities (30—60 mg.) of the acid for vapour-pressure studies were obtained by distilling the acid into small weighed flasks, sealing these under a vacuum, and re-weighing the pieces (correction for air displacement was made). The flasks containing the weighed sample of acid were designed so that they could be broken in the vacuum-system and the acid transferred to the reaction flask without coming in contact with the atmosphere. In order to obtain the much smaller samples of acid (2—18 mg.) required for the rate measurements, 100—200 mg. of acid were weighed out in the same way and then vapourised into a large space (5—6 l.) consisting of one large and several small bulbs connected by tubing and stopcocks. As the volume of each of the components of this system was known, a known amount of acid could be introduced into the reaction zone from one or more of the small bulbs. The vapour pressure of acid in the dispensing system was kept below 75% of the saturation pressure of the acid at room temperature in order to minimise adsorption. Careful titration of samples obtained in this way showed them to be within 1% of the expected values.

The methods for measuring vapour pressure and reaction rates were described previously.[3,5] In the present work the volumes of the reaction flask and solvent were, respectively, 75·3 and 25 ml. for vapour-pressure studies and 136 and 35 ml. for the rate measurements. Concentrations, unless otherwise stated, have been expressed as moles per l. of solution, calculated from the volume of solvent and the number of moles of reactant introduced into the reaction zone, and not from the amount of reactant in solution, except in the case of boron fluoride. The free (uncomplexed) boron fluoride is present largely in the gas phase; the dissolved but uncomplexed boron fluoride is always a constant fraction of this free boron fluoride—about 30% in the rate experiments—so its concentration, designated $[\mathrm{BF_3}]_{\mathrm{soln}}$, has been used throughout this work.

The reaction temperature was 20° in all cases.

Butene samples were analysed by gas–liquid chromatography on a column prepared from a mixture of 20% of propylene carbonate and 80% of firebrick (30—60 mesh) in 25 ft. of copper

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[4] Eastham, *J. Amer. Chem. Soc.*, 1956, **78**, 6040.

[5] Clayton and Eastham, *J. Amer. Chem. Soc.*, 1957, **79**, 5368.

tubing (0·25″ internal diameter) and operated at room temperature with helium as the carrier gas. Approximate retention times found were: n-butane, 9—10; but-1-ene, 14—15·5; isobutene, 15—16·5; *trans*-but-2-ene, 16—17·7; *cis*-but-2-ene, 18·5—20·5 min. Isobutene could thus interfere with the separations, but no trace of this isomer has been observed in our reaction mixtures. The column was calibrated over a wide range of synthetic mixtures of *cis*- and *trans*-but-2-ene and but-1-ene (a planimeter was used to evaluate the tracings), and the error in analysis found to be only ~1% and random. The Carroll method [6] for evaluating the chromatogram was useful for large samples but proved more erratic than the planimeter for the minor components.

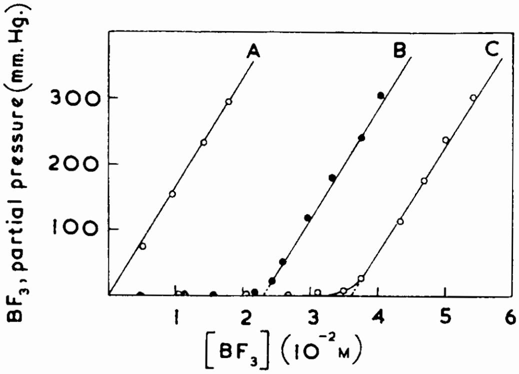


FIG. 1.

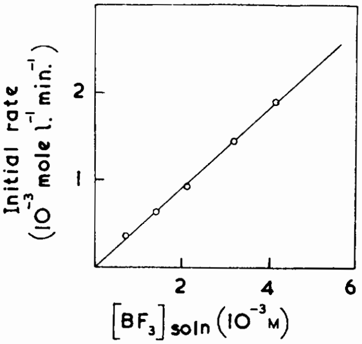


FIG. 2.

FIG. 1. AcOH = (A) 0·0, (B) 2·33, and (C) 3·358 × 10^{-2}M.

FIG. 2. Rate of formation of *trans*- from *cis*-but-2-ene (1·0M). $[BF_3,CH_3·CO_2H]$ = 1·31 × 10^{-3}M.

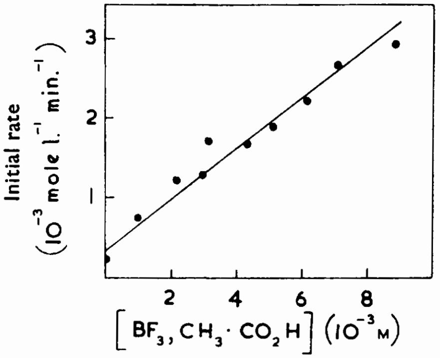


FIG. 3.

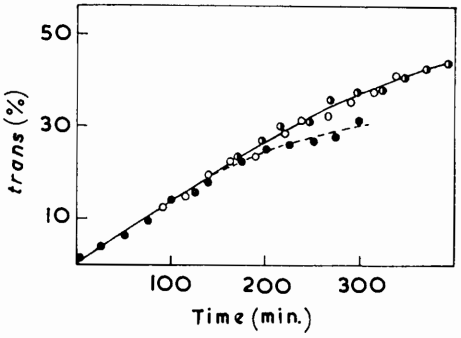


FIG. 4.

FIG. 3. Formation of *trans*- from *cis*-butene (1·0M). $[BF_3]_{soln}$ = 2·1 × 10^{-3}M.

FIG. 4. Initial olefin = (●) 100% *cis*, (○) 89·7% *cis* + 10·3% *trans*, (◑) 78·9% *cis* + 21·1% *trans*.

Results.—The partial pressures of boron fluoride over solutions of acetic acid in ethylene dichloride have been plotted against the total dissolved boron trifluoride, free and as complex, in Fig. 1. It is evident that, so long as the boron fluoride is somewhat (~10%) in excess of the acid, a 1 : 1 complex between catalyst and co-catalyst exists in solution but as the concentrations approach equality some dissociation of the complex may occur (compare the data [5] for BF_3–H_2O): $2BF_3,CH_3·CO_2H \rightleftharpoons BF_3 + BF_3,2CH_3·CO_2H$. For the present purpose it seems safe to assume that under the conditions of our rate measurements, the co-catalyst is present initially as this 1 : 1 complex.

[6] Carroll, *Nature*, 1961, **191**, 377.

The dependence of the rate of isomerisation upon catalyst and co-catalyst concentrations is shown in Figs. 2 and 3 where the initial rates of formation of *trans*-but-2-ene are plotted against the concentrations of the dissolved but free boron fluoride ($[BF_3]_{soln}$) and of acetic acid. In both cases the initial concentration of *cis*-but-2-ene was 1·01M. Within the limits of the experiments, the dependence is of the first order in each component of the catalyst system in agreement with our earlier observations on the methanol–boron fluoride catalyst system.

A significant " blank " is observed in these reactions in the absence of added co-catalyst (see Fig. 3). Its magnitude is roughly proportional to the boron fluoride concentration and, according to our earlier measurements which show that water is about thirty times as effective as acetic acid as a co-catalyst, could be accounted for if about 0·01 mg. of water were present in each reaction mixture. While this amount of adventitious water is not impossible, it seems rather high and, further, we have noticed that the blanks seem surprisingly similar, not only with different lots of purified reactants but also with different vacuum-systems and different operators. It may be, therefore, that they include some small amount of an un-cocatalysed or solvent-co-catalysed reaction or that the purification procedures leave a relatively constant amount of water or other co-catalyst in the reactants.

Because of the efficiency of the propylene carbonate column in separating the *cis*-but-2-ene and but-1-ene, it was possible to observe the formation of both the *cis*- and the *trans*-isomer from but-1-ene and hence to confirm effectively our earlier observation that the rates of formation of the two isomers are about equal. Table 1 shows results of experiments in which the concentrations of free boron trifluoride and of the complex $BF_3,CH_3{\cdot}CO_2H$ were, respectively, $2{\cdot}05 \times 10^{-3}$ and $1{\cdot}18 \times 10^{-3}$M. Over a thirty-fold range of concentration the rates of formation of the *cis*- and *trans*-isomers remain equal, and the rate of disappearance of but-1-ene changes by a factor of about three. The nature of the dependence upon initial concentration is discussed below.

TABLE 1.

Initial [but-1-ene] (mole $l.^{-1}$)	2·07	1·52	1·02	1·00	0·76	0·50	0·25	0·125	0·063
Initial rates of formation:									
cis-but-2-ene (10^{-4} mole $l.^{-1}$ min.$^{-1}$) ...	6·6	6·9	7·3	7·8	7·3	6·0	4·6	3·3	2·4
trans- ,, ,, ,, ...	6·5	6·6	7·9	7·8	6·9	6·1	4·6	3·3	2·3

In an effort to determine whether a reactive intermediate accumulates during the reaction, a few runs were carried out with identical catalyst concentrations but with synthetic mixtures of *cis*- and *trans*-isomers, as the olefin. Results obtained from reactions in which the starting mixtures were 100% *cis*, 89·7% *cis*–10·3% *trans*, and 79% *cis*–21% *trans* are shown in Fig. 4. It seems clear that the rate at any particular composition is the same whether the reaction is started with that composition or allowed to reach it by reaction, so we conclude that no build-up of reactive intermediate occurs.

n-Butenes can be converted into polymers of low molecular weight quite easily with these catalysts, as will be described in a later paper. In the present work polymerisation became appreciable only at the highest catalyst and monomer concentrations and is not believed to have any important bearing on the results reported here.

For reasons outlined above, the dependence of the rate of isomerisation upon butene concentration has been studied with particular care over a rather wide range of concentrations (0·03—2·6 mole $l.^{-1}$) for both the *cis*- and *trans*-but-2-ene, with results shown in Fig. 5 where the rates of isomerisation are plotted against butene concentration. In the earlier work our measurements were confined to the concentration range 0·2—2·0 mole $l.^{-1}$ and led us to the conclusion that the rates were essentially independent of olefin concentration, but it is now apparent that the rate increases sharply with butene concentration at concentrations below about 0·5 mole $l.^{-1}$ and then falls off again. Similar results were found with but-1-ene (Table 1).

The decrease in rate at the higher concentrations seems to be due to a medium effect resulting from the addition of the large amounts of olefin to the solvent since a similar effect can be produced by adding n-butane to the reaction mixtures (Table 2).

TABLE 2.

cis-But-2-ene, 0·50M; $BF_3,CH_3{\cdot}CO_2H$, $1{\cdot}05 \times 10^{-3}$M; $[BF_3]_{soln}$, $2{\cdot}08 \times 10^{-3}$M.

[n-Butane] (M)	0·0	0·49	1·02	1·53
Rate (10^{-4} mole $l.^{-1}$ min.$^{-1}$)	8·4	7·0	5·6	4·0

DISCUSSION

The foregoing results, obtained with acetic acid as co-catalyst, confirm our previous conclusion that the rate of isomerisation is directly dependent on the concentrations of both free boron fluoride and boron fluoride–co-catalyst complex but suggest strongly that the olefin concentration influences the rate through an equilibrium process. Unfortunately, in order to evaluate the equilibrium constant it is necessary to make two important corrections—for the medium effect and for the blank—and neither can be made with precision.

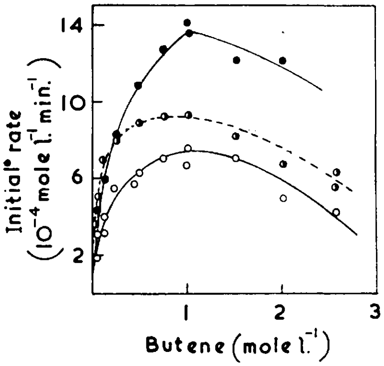


FIG. 5.

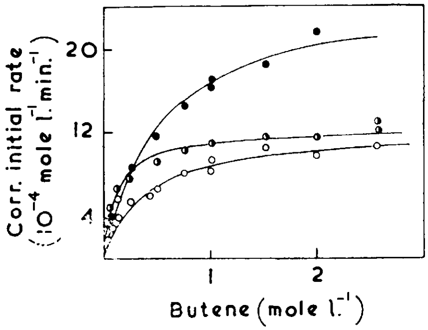


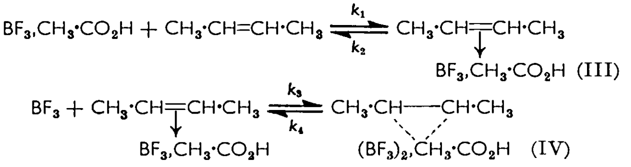
FIG. 6.

FIG. 5. ◑ *cis*-But-2-ene. ○ *trans*-But-2-ene. ● But-1-ene. $[BF_3,CH_3\cdot CO_2H] = 1{\cdot}1 \times 10^{-3}$M; $[BF_3]_{soln} = 2{\cdot}0 \times 10^{-3}$M.

FIG. 6. ◑ *cis*-But-2-ene. ○ *trans*-But-2-ene. ● But-1-ene. $[BF_3,CH_3\cdot CO_2H] = 1{\cdot}05 \times 10^{-3}$M; $[BF_3]_{soln} = 2{\cdot}1 \times 10^{-3}$M.

In correcting for the medium effect we have assumed that the retarding effect of the butenes is the same as that observed with butane and, further, that the slope of the approximately linear decrease in rate with increasing hydrocarbon content (Table 2) applies at all olefin concentrations so that the " true " rate can be obtained by extrapolation to zero hydrocarbon concentration. Correction for the blank was made by measuring the rates of isomerisation of both *cis*- and *trans*-but-2-ene in the absence of added co-catalyst. Since the rates thus obtained, though erratic, seemed to depend on the concentrations of free boron fluoride and of olefin in much the same way as did the co-catalysed reactions, correction was made by simply subtracting the estimated value of the blank from the observed rate. The corrected values for the rates are shown as the experimental points in Fig. 6.

The reaction parameters have been evaluated from the corrected experimental data on the basis of the following mechanism, where k_3 is the rate constant for the rate-controlling step:



$$BF_3,CH_3\cdot CO_2H + CH_3\cdot CH{=}CH\cdot CH_3 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \underset{\displaystyle BF_3,CH_3\cdot CO_2H\ \text{(III)}}{CH_3\cdot CH{=}CH\cdot CH_3} \qquad (6)$$

$$BF_3 + \underset{\displaystyle BF_3,CH_3\cdot CO_2H}{CH_3\cdot CH{=}CH\cdot CH_3} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \underset{\displaystyle (BF_3)_2,CH_3\cdot CO_2H\ \text{(IV)}}{CH_3\cdot CH{-}{-}CH\cdot CH_3} \qquad (7)$$

As noted earlier, this is the only mechanism we have been able to devise which accounts completely for all of our observations, while still obeying the laws of equilibrium. From the kinetic point of view it makes no difference whether isomerisation occurs in the formation or the rearrangement of complex (IV), so long as $k_3 \ll k_1, k_2, k_4$. The rate expression for this system, where the concentration of complex (IV) is always very much smaller than that of complex (III), must approximate closely to

$$\text{Rate of isomerisation} = \frac{k_3[\text{Butene}][BF_3]_{soln}[BF_3,CH_3\cdot CO_2H]}{K + [\text{Butene}]},$$

where $K = k_2/k_1$. In the general case, this equation should be modified to account for differences in the values of k_1, k_2, and k_3 for each isomer and to allow for the fact that the butene concentration is a composite one but, since in the present work we are dealing only with initial rates of a single isomer, the equation can be used in this form to obtain the constants for each isomer. It is evident that when the butene concentration is large compared to the value of K, the rate will reduce to $k_3[BF_3]_{soln}[BF_3,CH_3\cdot CO_2H]$ and an approximation to k_3 can be obtained. Similarly, an approximation to k_3/K can be obtained at low butene concentrations. Adjustment of these approximations to give the best agreement with experiment leads to the following values of the constants; the rates calculated from the constants are shown as the curves in Fig. 6.

	k_3 (10^2 l. mole^{-1} min.$^{-1}$)	K (mole l.$^{-1}$)
cis-But-2-ene	5·5	0·115
trans-But-2-ene	5·5	0·39
But-1-ene	11·5	0·52

The results for *cis*-but-2-ene and but-1-ene are in good agreement with the experimental values but those for *trans*-but-2-ene are less satisfactory. However, the experimental error is greatest for the *trans*-isomer because, since the equilibrium mixture contains 76% of this isomer, it is difficult to obtain rate measurements at sufficiently low conversions to avoid interference from the back-reaction.

It should be noted that while the values of k_3 suggest that but-1-ene reacts faster than *cis*- or *trans*-but-2-ene in the rate-controlling step, such is not the case. The product of the isomerisation of any of the isomers is primarily a mixture of the *cis*- and *trans*-isomers in about equal amounts, but since one observes only the formation of isomers different from the starting isomer the observed rate for but-1-ene will be the rate of appearance of both *cis* and *trans*, whereas the rate for *cis*- or *trans*-but-2-ene will be the rate of appearance of only one of these isomers. It follows that the rate constant for the passage of the *cis*- or *trans*-isomer through the reaction process will actually be double that shown and hence essentially identical with the value for but-1-ene. This similarity is disturbing since it suggests a rate-controlling step involving species in which configuration has already been lost and this is not that of the proposed mechanism. It may be, however, that attack by the free boron fluoride occurs at some point in the initial complex (III) which is not greatly influenced by the loosely held olefin.

A test of the constants can be obtained by calculating from them the composition of the mixture at equilibrium. This turns out to be *trans* 75%, *cis* 22%, and but-1-ene 2·8%, in good agreement with the corresponding values of 76%, 21·5%, and 2·8% estimated from the thermodynamic data.[7]

The above mechanism thus is in complete accord with all of our observations on the reaction; the only alternative to it seems to be some much more complex process yielding similar kinetics. If we assume that this simplest process is the most probable one, further progress in the study of these reactions can come only from more detailed knowledge of the intermediates in the process [complexes (III) and (IV)] and, while the present approach is not likely to yield such information, it does permit us to draw a few conclusions.

Complex (III) has been postulated as a loose complex between the olefin, the catalyst, and the co-catalyst, which forms and dissociates rapidly without loss of olefin configuration. It probably, though not necessarily, contains only one molecule of olefin and may be the π-complex frequently postulated in acid–olefin reactions.[8] It bears some resemblance to the complex observed between anhydrous perchloric acid and but-2-ene,[1] so perhaps can be regarded as a derivative of the acid HBF_3OH, but the spectra of the solutions, which are now under investigation, give little support to this view. Recent results at high catalyst concentrations suggest that complex (III) can lead to some

[7] Kilpatrick, Prosen, Pitzer, and Rossini, *J. Res. Nat. Bur. Stand.*, 1946, **36**, 559.

[8] Purlee and Taft, *J. Amer. Chem. Soc.*, 1956, **78**, 5811; Olah and Kuhn, *ibid.*, 1958, **80**, 6535.

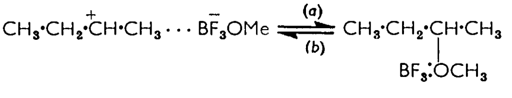
isomerisation and polymerisation, and there is good reason to believe that it will polymerise isobutene, but there is no doubt that complex (III) is less effective than complex (IV) in bringing about these reactions, by a factor of several powers of ten.

The formation of complex (III), as indicated by the values of K, is quite sensitive to the structure of the olefin; in fact, it is the relative extent of formation of this complex with the three isomers which governs the approach to equilibrium in the present system. We have been unable to isomerise *cis-* and *trans*-dichloroethylene with boron fluoride–methanol and tentatively ascribe the absence of reaction in this case to a low value of K for this olefin. More information is required on the ability of olefins to form complexes with acids.

The relation between the rate of isomerisation and the nature of the co-catalyst is curious since it does not seem to be directly related to the acidity of the co-catalyst. In the present work the relative rates obtained with the co-catalysts, water, acetic acid, and methanol, are about 50 : 1·5 : 1, and similar observations have been made with other reactions.[9] Since complex (III) seems to be formed to more or less the same extent with all of the co-catalysts, it follows that the nature of the co-catalyst governs the rate of subsequent steps in the reactions, *i.e.*, the formation or rearrangement of complex (IV). The stability of the anions derived from acids of the type $H{\cdot}CH_3O(BF_3)_2$ may be the factor which determines co-catalyst efficiency.

Little can be said about the nature of complex (IV). Brown, Stehle, and Tierney [10] have claimed that amines and boron fluoride form reasonably stable compounds of the type $R_3N,2BF_3$ both in the crystal and in solution, which suggests the possibility that complex (IV) is an oxygen analogue of such compounds. This view has some attraction since Barr, Gillespie, and Robinson [11] have shown that in a series of acids such as H_2O,xSO_3, acid strength increases with x and one might therefore argue that, of the acids H_2O,BF_3 and $H_2O,2BF_3$, the former is " strong " enough to polymerise isobutene but only the latter can protonate but-2-ene. However, there are a number of arguments against this view. " Acid strength " in its usual meaning would probably govern the formation of complex (III) and this reaction occurs readily with the first acid of the series. Furthermore, acids such as perchloric which are quite strong enough to produce isomerisation in aqueous solution (where the effective acid is the weaker H_3O^+) fail to bring about rapid isomerisation in ethylene dichloride although they do react or form complexes readily. Finally, recent nuclear magnetic resonance studies in these laboratories [12] have failed to confirm the existence, in solution, of complexes containing two molecules of boron fluoride per molecule of amine or ether, even at temperatures as low as —100°, although such complexes may exist in the crystal. It seems probable, therefore, that complex (IV) is present only in very low concentrations, perhaps only as a transition complex, and that the function of the second molecule of boron fluoride is to provide a reaction path which is otherwise not available in solvents such as ethylene dichloride.

One further point seems worth mentioning. If complexes (I) and (II) had structures of the type $R^+ \cdots CH_3O\bar{B}F_3$ and $R^+ \cdots CH_3\bar{O}(BF_3)_2$, as frequently suggested in the literature, one might expect them to rearrange readily to the ethers (reaction 8), and this



$$\mathrm{CH_3{\cdot}CH_2{\cdot}\overset{+}{C}H{\cdot}CH_3 \cdots \overset{-}{B}F_3OMe} \underset{(b)}{\overset{(a)}{\rightleftharpoons}} \mathrm{CH_3{\cdot}CH_2{\cdot}\underset{\displaystyle BF_3{:}OCH_3}{\underset{|}{C}}H{\cdot}CH_3} \qquad (8)$$

they do not seem to do. It is true that in the polymerisation, co-catalyst seems to be consumed and therefore reaction (8*a*) may constitute a termination process, but it does not seem important in isomerisation. We have, however, been disturbed by the fact that the

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[9] Satchell, *J.*, 1961, 3822.

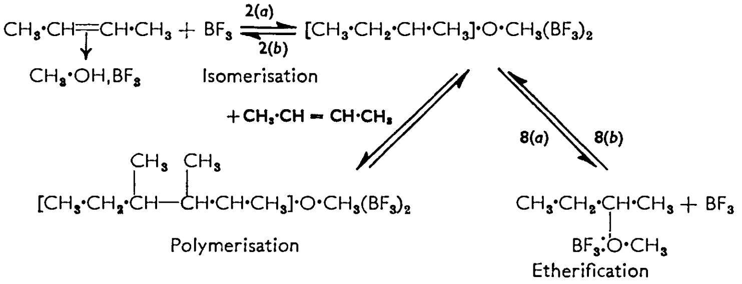
[10] Brown, Stehle, and Tierney, *J. Amer. Chem. Soc.*, 1957, **79**, 2020.

[11] Barr, Gillespie, and Robinson, *Canad. J. Chem.*, 1961, **39**, 1266.

[12] Brownstein, Eastham, and Latremouille, unpublished work.

decomposition of ethers by boron fluoride shows some marked similarity to the isomerisation.[13] Ethers containing only primary alkyl groups are quite stable to boron fluoride, and those containing a tertiary group are decomposed by an equimolar amount of that reagent, but an ether such as 2-methoxybutane is stable as the 1 : 1 complex and decomposes in the presence of an excess of boron fluoride. These conditions, although found at much higher catalyst concentrations, are so similar to those for polymerisation and isomerisation that they suggest a common intermediate and a reaction scheme of the type shown.

For a scheme of this kind to apply, both reactions (8*a* and *b*) must be very slow since the ether does not act as a co-catalyst and the co-catalyst is not consumed rapidly in the isomerisation. We are inclined to believe, however, for the following reasons, that etherification proceeds by a different process. In the first place, 2-methoxybutane can be prepared from those reagents, but the reaction is exceedingly slow and optimum conditions require high concentrations and a ratio of methanol to boron fluoride of about 2 : 1. Admittedly these may be conditions for an alternative reaction path in which etherification is favoured over isomerisation and polymerisation, so they do not necessarily rule out reaction (8*a*). In the second place, the reaction conditions for decomposition of the ether may be identical with conditions for polymerisation because polymerisation of the resulting olefin is the driving force of the decomposition. In all of our experiments with ether decomposition, the yield of alcohol was essentially quantitative but the olefin was recovered primarily (but not completely) as polymer. We are therefore inclined to the view that equilibrium between etherification and de-etherification does exist but greatly favours the ether, that it probably does not involve the same intermediates as function in polymerisation and isomerisation, and that de-etherification is accomplished only when the resulting olefin can be polymerised as formed.



Finally, it seems worth noting that olefin–boron fluoride–acetic acid solutions show an absorption band at about 300 mμ. Bands in this region have been attributed by various authors to aliphatic carbonium ions,[14] although the evidence for such a view is not conclusive and the wavelength seems remarkably long for such species. In the present case, studies now under way indicate that the chromophore, whatever its nature, is not due directly to the active intermediates because that band grows steadily over a much longer period of time than is required for isomerisation and shows an induction period. Since we have already shown that there is no build-up of active intermediate during the reaction, it seems clear that the chromophore is the product either of a parallel or, more probably, of a secondary reaction, perhaps involving the active intermediates.

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[13] Eastham and Latremouille, unpublished work.

[14] Rosenbaum and Symons, *Mol. Phys.*, 1960, **3**, 205; Deno, Richey, Hodge, and Wisotsky, *J. Amer. Chem. Soc.*, 1962, **84**, 1498.