46. *Co-catalyses in Friedel–Crafts Reactions. Part VII.*[1] *The Formation of Ultraviolet Chromophores.*

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Solutions of butene in ethylene dichloride with boron trifluoride and hydroxylic co-catalysts slowly develop an absorption band with a peak at 304 ± 2 mμ, in addition to isomerising and polymerising. The kinetics of peak growth show that the band is not due to an intermediate in the isomerisation or polymerisation reactions, but may be due to alkylated alkenyl cations, formed by hydride abstraction from butene or unsaturated polybutene by aliphatic carbonium ions. The ultraviolet spectra obtained from conjugated dienes in acid solutions closely resemble those obtained from butene in the solutions described above.

The formation of species giving rise to ultraviolet absorption spectra from hydrocarbons and acids has received much attention recently. Rosenbaum and Symons,[2] and Oláh,[3] report spectra in sulphuric acid and in antimony pentafluoride with peaks at 291 and 292 mμ, respectively, which they ascribe to the tertiary butyl carbonium ion, but they obtain widely different extinction coefficients for the ion. Deno [4] gives evidence that cyclopentenyl cations absorb at 270—300 mμ, cyclohexenyl cations at 315—320 mμ, and linear alkenyl cations at 305—307 mμ in sulphuric acid. The extinction coefficients of all these ions vary from 5×10^3 to 14×10^3 and usually approximate to 10^4.

During recent experiments on the isomerisation of butene using boron trifluoride and acetic acid as catalysts and ethylene dichloride as solvent,[5] the slow development of an absorption peak in the ultraviolet region with a maximum at 304 ± 2 mμ was noted. This was found to be a general phenomenon in systems containing boron trifluoride and a hydroxylic co-catalyst when the boron trifluoride to acetic acid ratio was greater than one. If that ratio became appreciably less than one the peak at 304 ± 2 mμ was not formed, and also the major reaction products were different.

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[1] Part VI, Allcock and Eastham, *Canad. J. Chem.*, 1963, **41**, 932.
[2] Rosenbaum and Symons, *Mol. Phys.*, 1960, **3**, 205.
[3] Olah, Tolgyesi, Kuhn, Moffatt, Bastien, and Baker, *J. Amer. Chem. Soc.*, 1963, **85**, 1328.
[4] Deno, Bollinger, Friedman, Hofer, Hodge, and Hauser, *J. Amer. Chem. Soc.*, 1963, **85**, 2998.
[5] Clayton and Eastham, *J.*, 1963, 1636.

When the reagent concentrations were $<10^{-2}$ mole l.$^{-1}$ of the boron trifluoride-acetic acid complex (BFA), $<5 \times 10^{-2}$ mole l.$^{-1}$ of (boron trifluoride)$_{\text{soln.}}$, and 0·1—2·0 mole l.$^{-1}$ butene, the peak at 304 ± 2 mμ was the only one formed rapidly; when 0·1—0·5 mole l.$^{-1}$ BFA and approximately 1·0 mole l.$^{-1}$ butene were used, peaks also appeared in the visible at 386, 472 and 572 mμ. These last were very similar to the peaks obtained by Tauber and Eastham[6] from butene with sulphuric or perchloric acids in ethylene dichloride solution, and will be the subject of a subsequent Paper. This report is concerned with the kinetics of peak growth at 304 ± 2 mμ in solutions containing 10^{-3}—5×10^{-2} mole l.$^{-1}$ BFA, 10^{-3}—10^{-2} mole l.$^{-1}$ (boron trifluoride)$_{\text{soln.}}$, and 0·1—2·0 mole l.$^{-1}$ butene.

EXPERIMENTAL

Ethylene dichloride, the butene isomers, boron trifluoride, and acetic acid were manipulated as described previously.[5,7] Butadiene was dried rapidly over sodium, then stored and used similarly to butene; 2,4,4-trimethylpent-1-ene was dried over sodium, distilled, stored on the vacuum line over sodium, and manipulated in weighed ampoules in the manner previously described for acetic acid. 3,4-Dimethylhexa-2,4-diene, which could be formed in the reaction mixtures from but-2-enes, was prepared by the method of McCallum and Whitby;[8] the product contained some olefins and paraffins. 2,5-Dimethylhexa-2,4-diene obtained commercially was over 99% pure after distillation. The dienes were manipulated as gases in the vacuum system; Plesch–Biddulph valves[9] were used for the gas measurement to prevent absorption of the dienes by tap grease.

For most of the reactions 15—30 mg. of acetic acid were required, but as these weights could not be accurately reproduced, the acid was weighed first, and the quantities of solvent, butene, and boron trifluoride adjusted to give the required concentrations. Allowance was made for the quantity of boron trifluoride in the gas phase, and the subscripts " total," " free," and " soln." were used as previously described for the boron trifluoride concentrations.[5,7]

The reaction vessel consisted of a round-bottomed bulb containing a stirring magnet, with a 1 cm. rectangular quartz cell attached through a side arm; a " spacer " was used to cut the optical path length to 1 mm. for very rapid reactions. The solution volume was about 15—25 ml., and the total volume of the vessel was *ca.* 75 ml. The reagents entered the flask through a long glass spiral on a horizontal axis which prevented the entry of tap grease. The flask was sealed under vacuum after filling.

The solutions in sulphuric acid solvent were made up by pipetting the acid (Baker and Adamson " CP ") into the flask through a side arm which was then sealed. The acid was degassed, then the gaseous butene was absorbed into the stirred acid. Finally, the flask and contents were frozen and sealed under vacuum. It was hoped that unduly high local concentrations of hydrocarbon would be avoided by this technique.

The spectra of the solutions were obtained with a Beckman DK 1 and (mainly) with a Carey 14 recording spectrophotometer. Cell path lengths, calibrations, etc., were obtained by standard methods. Butene, boron trifluoride, and acetic acid individually had negligible adsorption above 240 mμ (the " cut-off " wavelength for ethylene dichloride). BFA had a weak absorption, $\lambda_{\text{max.}} = 285$ mμ, $\varepsilon_{\text{max.}} = 0{\cdot}5$, which was negligible under reaction conditions.

The rate of peak formation was followed at room temperature; the reproducibility of the results indicated that the reaction was not sensitive to small temperature change. " Zero time " of the reaction was taken when all the reagents melted.

The polymerisation of butene was followed by the vapour pressure drop in a closed system using a capillary manometer. The reaction temperature was 20° and " zero time " was taken from the instant all the reagents melted. The quantity of unreacted butene was estimated directly from the vapour pressure of the solution, and the polymer was estimated as (reacted butene)/4, since the average chain length of polymer under similar conditions has been found to be about four monomer units.[1]

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[6] Tauber and Eastham, *J. Amer. Chem. Soc.*, 1960, **82**, 4888.

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

[8] McCallum and Whitby, *Trans. Roy. Soc. Canada*, 1928, **3**, 39.

[9] Biddulph and Plesch, *Chem. and Ind.*, 1956, 569.

RESULTS

The rate of peak growth in reactions which reproduced the isomerisation conditions [5] proved to be very slow and erratic, therefore the concentration of BFA was raised from $0{\cdot}1 \times 10^{-2}$ to $2{\cdot}0 \times 10^{-2}$ mole l.$^{-1}$, while the concentration of butene was varied from 0·1 to 2·0 mole l.$^{-1}$, and that of (boron trifluoride)$_{\text{soln.}}$ from 10^{-3} to 10^{-2} mole l.$^{-1}$.

The solutions were initially transparent throughout the ultraviolet spectrum, then a peak began to grow at 304 ± 2 mμ. The rate of the peak growth increased with time for the first 10—70 min. of reaction, then remained constant for at least 30—60 min. and usually until the optical density of the peak became too high for measurement. From this steady period of reaction a rate was calculated by dividing increase in optical density by the time of the increase. Occasionally when a path length of 1 mm. was used, it could be seen that the reaction rate finally began to decrease, especially if the BFA concentration was low initially, indicating that the acid was being consumed in the system. The rates obtained during the period of constant growth were reproducible within 7% for all systems.

The induction period of the reaction could be related to the behaviour of the butene in the mixture. While the reagents were being warmed to room temperature and for 10—30 min. afterwards some polymerisation took place; after this time polymerisation continued but the rate usually fell off considerably. The induction period corresponded approximately to this period of initial rapid reaction. The constant growth took place when considerable amounts of polymer were present (often about 25—35% of the initial butene), and when the rate of polymerisation was so slow that the concentrations of monomeric and polymeric butenes were virtually constant.

These results suggested that polymer was necessary for peak growth. To test this, 2,4,4-trimethylpent-1-ene (di-isobutene, TMP) was added to several reaction mixtures in which the catalyst concentrations were $2{\cdot}0 \times 10^{-2}$ mole l.$^{-1}$ BFA and $2{\cdot}5 \times 10^{-3}$ mole l.$^{-1}$ (boron trifluoride)$_{\text{soln.}}$ and the proportion of TMP was increased from 0 to 90% of the total weight of hydrocarbon present, the remainder being *cis*-but-2-ene. The rate isomerisation was found to be considerably retarded by increasing weights of hydrocarbon,[5] the hydrocarbon weight was held approximately constant and equal to $[0{\cdot}3 \pm 0{\cdot}05]$ mole l.$^{-1}$ of TMP. Under similar catalyst conditions in reaction mixtures containing pure butene, there is about 5% polymerisation after the first 10 min. of reaction, the rate of peak growth is very small, and the total induction period is 40—50 min. Thus, it was possible to estimate the behaviour of the TMP separately from that of the polybutene by studying the rate of peak growth in the first 10 min. of the reaction. In all the reactions containing TMP a linear rate of peak growth took place initially. Afterwards, the rate of peak growth increased if the percentage of TMP present was small, but the rate remained steady throughout the period of observation if the TMP concentration was greater than 80% of the hydrocarbon. Furthermore, it was noted that the rate of peak growth during the first few minutes of the reaction was approximately proportional to the square root of the TMP present initially. The results confirm that in solutions containing butene alone, polymer is probably necessary for chromophore production.

Fig. 1 shows the rate variation with initial *cis*-2-butene in a series of reactions where the catalyst concentrations were held constant (the full circles connected by a broken curve). A maximum in the rate of peak growth was observed at 0·7 mole l.$^{-1}$ *cis*-but-2-ene; above this concentration the rate decreased with increasing hydrocarbon concentration. As in the isomerisation experiments,[5] a considerable retardation of the reaction was produced by addition of *n*-butane to these systems, and corrections for this effect were applied as explained previously. The corrected curve in Fig. 1 (the triangles connected by a solid curve) shows that the reaction rate becomes virtually independent of the initial *cis*-but-2-ene concentration at high concentration.

The quantities of butene and polybutene present in each reaction during the period of constant rate of peak growth were calculated, and [butene], [polybutene], and $[\text{polybutene}]^{\frac{1}{2}}$ were plotted against the rate. The results indicated that the order in hydrocarbon was not simple; a more complex rate equation is developed in the Discussion.

The dependence of the rate on (boron trifluoride)$_{\text{soln.}}$ and BFA concentrations were obtained from two series of reactions where the initial concentration of one of the catalysts was varied; the other catalyst and the butene concentrations were held constant. The rate dependence appeared to be of the first order in (boron trifluoride)$_{\text{soln.}}$ and approximately 1·7th order in

BFA. As the polymer concentrations were not identical for all the reactions at the period when the constant rate was measured, the apparent orders may not be exact. However, several of the reactions in each series were calculated to have contained similar amounts of polymer during the period that the rate was measured; thus a rough guide to the orders in the catalysts was obtained.

cis-But-2-ene was used for the reactions discussed above; *trans*-but-2-ene and but-1-ene showed the same general behaviour. The rates obtained for *trans*-but-2-ene appeared to be about 10% lower than the corresponding values for *cis*-but-2-ene (Fig. 1), perhaps because of the slightly lower rate of polymerisation of the *trans*-isomer.

As the tertiary butyl carbonium ion has been reported to have an ultraviolet spectrum with $\lambda_{max.}$ at 294 ± 3 mμ in sulphuric acid and also in antimony pentafluoride,[2,3] the behaviour of isobutene in boron trifluoride, acetic acid, and ethylene dichloride systems was studied. When the isobutene content of the system exceeded 0·1 mole l.$^{-1}$, at the usual catalyst concentrations, a gelatinous precipitate of polymer formed instantly. When (10^{-3}—10^{-4}) mole l.$^{-1}$ isobutene and 0·1 mole l.$^{-1}$ BFA were used, a spectrum with a major peak at 285 mμ was obtained. This peak grew rapidly for the first few minutes of the reaction, then very slowly for many days. The apparent extinction coefficient (calculated by dividing the optical density value obtained when the peak growth had virtually ceased by the initial isobutene concentration) increased from 600 to 1300 as the concentration of isobutene decreased from 13 × 10^{-4} to 3 × 10^{-4} mole l.$^{-1}$, and minor peaks were observed in the spectra. It appeared that polymerisation was taking place even under these conditions; Deno[10] found that the 1,3-dimethylcyclopentadiene dimerised even in 10^{-5} mole l.$^{-1}$ concentration in 35% sulphuric acid. It is possible that the 285 mμ peak is due to the tertiary butyl carbonium ion, but if so, this cannot be the chromophore formed in systems containing normal butenes.

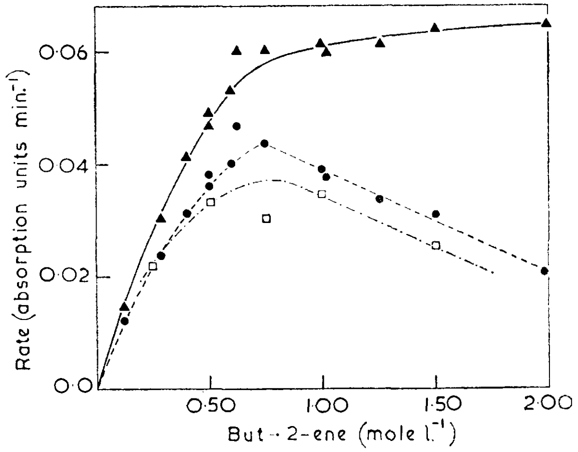

FIG. 1. The variation of rate with butene concentration.
[BF_3–CH_3·CO_2H] = 2·0 × 10^{-2} mole l.$^{-1}$; [BF_3]$_{soln.}$ = 2·5 × 10^{-3} mole l.$^{-1}$.
● *cis*-But-2-ene experimental results.
□ *trans*-But-2-ene experimental results.
△ *cis*-But-2-ene corrected results.

*The Spectra of Dimethylhexa-*2,4-*dienes.*—Deno[4] found linear alkenyl cations to have absorption maxima at 305—307 mμ in sulphuric acid. The acid and neutral spectra of 3,4-dimethyl- and 2,5-dimethyl-hexa-2,4-dienes were obtained in solutions containing 10^{-3}—19^{-4} mole l.$^{-1}$ diene and *ca.* 0·1 mole l.$^{-1}$ BFA.

Impure 3,4-dimethylhexa-2,4-diene has a peak in ethylene dichloride solution at 250 mμ which vanishes on addition of BFA and a new peak appears at 315 mμ. Pure 2,4-dimethylhexa-2,4-diene has a peak at *ca.* 245 mμ in ethylene dichloride and a peak at 307 mμ on addition of BFA. The latter, like the isobutene peak, grew rapidly for the first few minutes of reaction and slowly afterwards. The apparent extinction coefficient increased from 7500 to 11,000 when the initial diene concentration decreased from 13 × 10^{-4} to 4·5 × 10^{-4} mole l.$^{-1}$, indicating that polymerisation was again reducing the amount of chromophore present. The extinction coefficient of the chromophore, which is thought to be the alkenyl cation $(CH_3)_2CH\overset{+}{\overbrace{CH\!=\!=\!CH\!=\!=\!C}}(CH_3)_2$, probably approaches 1·2 × 10^4 at infinite dilution. This $\varepsilon_{max.}$,

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[10] Deno, Richey, Friedman, Hodge, Hauser, and Pittman, *J. Amer. Chem. Soc.*, 1963, **85**, 2991.

and the $\lambda_{max.}$ of 307 mμ, agree well with those reported by Deno [4] for other aliphatic alkenyl ions. The spectrum from 2,5-dimethyl-2,4-hexadiene was very similar to that obtained from the butene system (Fig. 2), and the ion derived from the diene is thought closely to resemble in structure the chromophores produced from normal butene polymers.

Spectra in Sulphuric Acid.—Rosenbaum and Symons [2] report that isobutene instantaneously gives a stable peak, $\lambda_{max.} = 291$ mμ, $\varepsilon_{max.} = 6{\cdot}0 \times 10^3$, in sulphuric acid. In our experiments *cis*-but-2-ene gave a spectrum in sulphuric acid in which a peak at 295 mμ grew in the manner described above for isobutene and the dienes. In contrast to those systems, however, the apparent extinction coefficient increased from 1000 to 2500 when the *cis*-but-2-ene concentration was raised from $0{\cdot}5 \times 10^{-3}$ to $2{\cdot}4 \times 10^{-3}$ mole $l.^{-1}$. These results suggest that the *cis*-but-2-ene molecules reacted with each other to form a chromophore the nature of which was not investigated further.

*Reactions with Buta-*1,3*-diene.*—In the Discussion it is proposed that alkenyl ions are formed from butene and polybutene by hydride transfer. Alkenyl ions with terminal alkyl groups appear to be fairly stable from the dimethylhexadiene studies, but butadiene is known to polymerise rapidly in acid solutions suggesting that the butenyl cation is not stable. The behaviour of this ion under the experimental conditions was studied by adding small quantities of butadiene to the reacting systems. Pure butadiene polymerised rapidly even in 10^{-3} mole $l.^{-1}$ concentration in boron trifluoride-BFA solutions; however, similar quantities of the diene ($0{\cdot}3$—4×10^{-3} mole $l.^{-1}$) markedly accelerated the formation of an ultraviolet peak at 310 mμ in solutions containing 0·5 mole $l.^{-1}$ *cis*-but-2-ene, $2{\cdot}5 \times 10^{-3}$ mole $l.^{-1}$ (boron trifluoride)$_{soln.}$, and $2{\cdot}0 \times 10^{-2}$ mole $l.^{-1}$ BFA. There was no induction period and the rate of peak formation increased linearly with the buta-1,3-diene concentration during the first few minutes of the reaction, when little absorption was produced by a similar reaction system containing only butene. The initial rate of a reaction containing 10^{-3} mole $l.^{-1}$ buta-1,3-diene was equivalent to the constant rate developed after an induction period in a similar catalyst system containing initially only 0·5 mole $l.^{-1}$ butene. The peak shape closely resembled that obtained from pure butene (although the maximum was at a slightly higher wavelength), and even when the initial diene concentration was increased to 4×10^{-2} mole $l.^{-1}$ there was no evidence of the peak broadening which accompanied the self-polymerisation of buta-1,3-diene. These results show that although the butenyl ion is unstable, it reacts in the presence of excess butene and polybutene to give chromophores which contribute to the major peak of the system. Thus, there is no practical reason to exclude a mechanism of chromophore production which involves the intermediate formation of a butenyl ion.

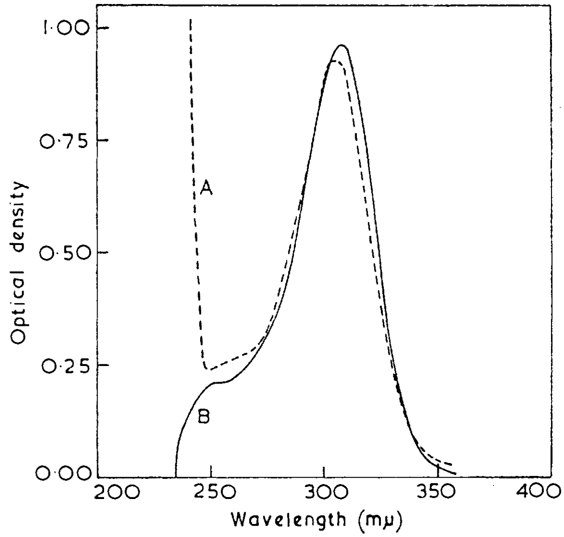

Fig. 2. Comparison of spectra.

A, typical spectrum from reaction containing *cis*-but-2-ene.

B, 2,5-Dimethylhexa-2,4-diene ($1{\cdot}3 \times 10^{-3}$ mole $l.^{-1}$) in BFA–ethylene dichloride solution (1 mm. cell).

DISCUSSION

Ultraviolet spectra with peaks at 300 ± 10 mμ have been recorded in systems containing alkyl fluorides and boron trifluoride,[11] and butene with fluorosulphonic,[12] fluorophosphoric,[12] and sulphuric acids [6] in methylene chloride or ethylene dichloride solutions, in addition to the present systems. The wide range of acids which cause ultraviolet peak formation suggests that these acids are acting solely as proton donors.

The induction period in the butene reactions and the growth of the peak over a longer period of time than would be required to isomerise the butenes indicate that the chromophores are not rapidly formed intermediates of the type required by the isomerisation and polymerisation reactions.[1,5] Also, the quantity of the chromophore in the systems was not related directly to the individual concentration of any of the butene isomers, or to total [monomer] or [polymer], and could not be due to minute traces of isobutene as this does not give a peak at 304 ± 2 mμ in reaction conditions. It is unlikely, therefore, that the chromophores are alkyl carbonium ions, for if this were so the chromophore concentration would be expected to be dependent on [monomer] and/or [polymer], as the equilibrium

$$R_2C{:}CR_2 + H^+ \rightleftharpoons R_2CHC^+R_2$$

if usually considered to be set up instantaneously. If such ions exist in the isomerisation or polymerisation reactions they must be present in low quantities and/or absorb light below 240 mμ.

The dimethylhexa-2,4-dienes instantaneously gave spectra in boron trifluoride–acetic acid catalyst systems which closely resembled those obtained from normal butenes in such conditions. Deno [4] found very similar spectra for other alkenyl cations in pure sulphuric acid. The dimethylhexenyl ions, formed from the pure compound, do not appear to decompose rapidly, and there is no indication that the addition of butene or polybutene adversely affects the stability of the alkenyl ions. It is therefore probable that the peak developed from the n-butenes is due to linear alkenyl ions, of the general formula $\overbrace{R_2C{=}CR{=}CR}^{+}{-}CHR_2$. The composition of the R-groups, provided that they are saturated alkyl residues, probably has little effect on the position of the peak maximum. The observed peak may well be a composite one, with many different alkenyl ions contributing.

Mechanism of Formation.—The phenomenon of hydride transfer is well known in acid solutions of hydrocarbons (see, *e.g.*, Deno *et al.*[13]) and can take place with amazing rapidity. In the usual form of the reaction, a carbonium ion withdraws a hydride ion from a hydrocarbon molecule to form a more stable ion. In the present systems a minute quantity of saturated carbonium ions may be formed, and this may then abstract hydride from the olefins (butene or unsaturated polybutene) present to form more stable alkenyl ions

$$R_3C^+ + R_2CHCR{:}CR_2 \longrightarrow R_3CH + R_2\overbrace{C{=}CR{=}CR_2}^{+} \tag{1}$$

$$R_3C^+ + CH_3CH{:}CHCH_3 \longrightarrow R_3CH + CH_3{-}\overbrace{CH{=}CH{=}CH_2}^{+} \tag{2}$$

then

$$CH_3{-}\overbrace{CH{=}CH{=}CH_2}^{+} + R_2C{:}CR_2 \xrightarrow{(a)} CH_3CH{:}CHCH_2CR_2\overset{+}{C}R_2$$

$$\xrightarrow{(b)} CH_3{-}\overbrace{CH{=}CH{=}CH}^{+}CR_2CHR_2 \tag{3}$$

($R_2C{:}CR_2$ is butene or polybutene).

Tertiary carbonium ions are considered to be much more easily formed than secondary ions, and as carbonium ions are the hydride acceptors, systems capable of giving tertiary

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[11] Woolhouse, unpublished work.

[12] Chapman, unpublished work.

[13] Deno, Petersen, and Saines, *Chem. Rev.*, 1960, **60**, 7.

carbonium ions are found to undergo hydride transfer reactions more readily than those giving only secondary ions.[13] Thus it appears likely that the increased rate of reaction observed in the presence of 2,4,4-trimethylpent-1-ene and polybutene is due to their providing a source of tertiary ions. Also, no butane was found in the reaction products indicating that the n-butyl carbonium ion, if formed, was not acting as a hydride acceptor. The formation and reaction of the unstable butenyl ion are shown in equations (2) and (3).

Agreement with Kinetic Results.—The extinction coefficient of alkenyl ions [4] is usually about 10,000, and using this figure for the extinction coefficient of the chromophore, it was calculated that less than 2% of the boron trifluoride–acetic acid complex could be bound to the chromophore as an anion during the period of steady reaction. Free boron trifluoride is not involved in the final product. Thus the rates were measured when the catalysts were present in virtually their initial concentrations. The average values of [butene] and [polybutene] were calculated for each system for the periods of constant rate measurement.

In several systems in which the formation of a carbonium ion is effected by an acid in a solvent of low dielectric constant, a high order in the acid component has been found,[14] and this was usually ascribed to the necessity of solvation of the anion. These reactions involved a step represented by

$$\mathrm{R_2C{:}CR_2 + 3AH \longrightarrow R_2\overset{+}{C}CHR_2 + A^-(2AH)_{soln.}} \tag{4}$$

The present reactions, and also the polymerisation of propylene using boron trifluoride and methanol as catalysts,[15] appear to have an order of approximately 1·5 in the boron trifluoride-co-catalyst complex, and it may be suggested that they also contain a step similar to (4).

The action of boron trifluoride as a catalyst is not yet understood. In all the isomerisation-, polymerisation-, and chromophore-producing systems the free boron trifluoride is a catalyst with a first-order effect. It may be that it stabilises ionic intermediates in some way.

In the following scheme: butene is represented by M, unsaturated polybutene by P, polybutene carbonium ion by P^+, saturated polymer by PH, butenyl ion by B^+, aliphatic alkenyl ion by D^+, and the BFA complex by A; and the subscript O indicates the initial concentration of the reagent.

$$\begin{array}{lll r}
M + A \rightleftharpoons MA & \text{rapid equilibrium} & [M][A] = K_M[MA] & (5)\\
P + A \rightleftharpoons PA & \text{,, \quad ,,} & [P][A] = K_P[PA] & (6)\\
MA + 2A \rightleftharpoons M^+ + A_3^- & \text{,, \quad ,,} & [MA][A]^2 = K_-[M^+][A_3^-] & (7)\\
PA + 2A \rightleftharpoons P^+ + A_3^- & \text{,, \quad ,,} & [PA][A]^2 = K_+[P^+][A_3^-] & (8)\\
\left.\begin{array}{l} P^+ + M \xrightarrow{k_1} PH + B^+ \\ P^+ + P \xrightarrow{k_2} PH + D^+ \end{array}\right\} & \begin{array}{l}\text{slow, rate determining}\\ \text{,, \quad ,, \quad ,,}\end{array} & & \begin{array}{r}(9)\\(10)\end{array}\\
\left.\begin{array}{l} B^+ + M \longrightarrow D^+ \\ B^+ + P \longrightarrow D^+ \end{array}\right\} & \text{formation of stable ion} & & \begin{array}{r}(11a)\\(11b)\end{array}\\
D^+ + A_3^- \rightleftharpoons DA + 2A & \text{rapid equilibrium} & [DA][A]^2 = K^*[D][A_3^-] & (12)\\
DA \rightleftharpoons D + A & \text{,, \quad ,,} & [D][A] = K_1[DA] & (13)
\end{array}$$

No attempt has been made to add free boron trifluoride to this scheme. The compounds MA, PA, and DA are probably partially ionic in character; this ionic character will increase

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[14] Evans, Jones, and Thomas, *J.*, 1957, 104; Mayo and Katz, *J. Amer. Chem. Soc.*, 1947, **69**, 1339; Mayo and Savoy, *ibid.*, 1947, **69**, 1348; Dewar, *ibid.*, 1963, **85**, 2248.

[15] Szell, unpublished work.

with the stability of the carbonium ions, and DA is probably almost entirely ionic (as the neutral peaks characteristic of the neutral hexadienes vanish on addition of BFA). It is assumed that D^+ and DA have similar spectra, both contributing to the peak at 304 ± 2 mμ.

From the results of previous isomerisation and polymerisation work, equilibria (5) and (6) are believed to be established rapidly. The ionisations (7) and (8) would be expected to be rapid; the kinetics indicate that they cannot be the rate determining steps. The absence of butane from the reaction product indicates that no hydride is abstracted by the secondary butyl ion. As this ion would be expected to be of high energy and reactivity if formed it is assumed that the amount of the secondary ion M^+ is negligible with respect to the tertiary ion P^+ and the effect of M^+ is ignored in the kinetic equation. The relative concentrations of D and P at the period of steady reaction make it reasonable to ignore the effect of the free ion D^+ in the reaction mixture. Reactions (9), (10), and (11) correspond to (1), (2), and (3), while (9) and (10) are rate determining.

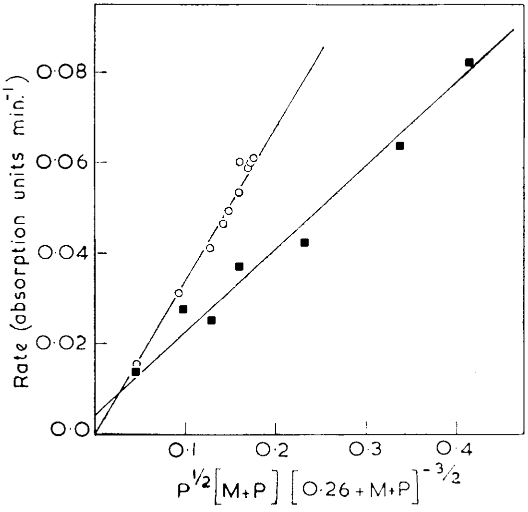

FIG. 3. Reaction rates in constant catalyst conditions.
$[BF_3-CH_3\cdot CO_2H] = 2\cdot0 \times 10^{-2}$ mole l.$^{-1}$; $[BF_3]_{soln.} = 2\cdot5 \times 10^{-3}$ mole l.$^{-1}$.
Initial olefin: ○ *cis*-But-2-ene; ■ *cis*-But-2-ene + 2,4,4-trimethylpent-1-ene.

Assuming that the order in free boron trifluoride is unity, the rate equation for the above reaction scheme may be shown to be

Rate of peak formation =

$$[BF_3]_{soln.}[K_PK_+]^{-1}A_O{}^{\frac{3}{2}}P^{\frac{1}{2}}[k_1M + k_2P] \times \{1 + M/K_M + P/K_P\}^{-\frac{3}{2}} \qquad (14)$$

In the above equation k_1, k_2, and K_P (as well as the constant $[K_PK_+]$) are unknown. K_M may be calculated [5] to be 0·26 mole l.$^{-1}$ for the equilibrium mixture of normal butene isomers. From the polymerisation results,[1,15] it seems likely that $K_M \leqslant K_P$, and probably $K_M \simeq K_P$ within an order of magnitude. Also, general consideration of the present systems indicates that k_1 may approximate to k_2. All the permutations of $K_P = K_M$, $K_P \gg K_M$, $k_1 \gg k_2$, $k_1 = k_2$, and $k_1 \ll k_2$ were tested in equation (14), and only the assumptions that $k_1 = k_2$ and $K_M = K_P$ gave consistent results for the constant $[K_MK_P]^{-1}$ for all the reactions in which the catalyst concentrations remained constant. The rate equation is now reduced to

$$\text{Rate of peak growth} = k_O[BF_3]_{soln.}A_O{}^{\frac{3}{2}}P^{\frac{1}{2}}[M + P][0\cdot26 + M + P]^{-\frac{3}{2}} = k_O\alpha \qquad (15)$$

The hydrocarbon term $P^{\frac{1}{2}}[M + P][0\cdot26 + M + P]^{-\frac{3}{2}}$ was calculated for all the reactions containing butene and 2,4,4-trimethylpent-1-ene in constant catalyst conditions. Fig. 3 shows the linear variation of the rate with the hydrocarbon term in these reactions; the corrected rate is plotted for the butene reactions. The scatter in the TMP results is probably due to the difficulty of estimating the rate correctly over a short time. The apparent half-order dependence on TMP mentioned earlier is due to several of the reactions taking place when [TMP] $\ll$ [approximately constant monomeric butene]. In such cases the hydrocarbon term becomes proportional to $[\mathrm{TMP}]^{\frac{1}{2}}$. For all the reactions where one of the catalysts was varied, (α) in equation (15) was calculated and plotted against the observed rate, in Fig. 4. The circles and triangles denote the series of experiments where $[\mathrm{BF}_3]_{\mathrm{soln.}}$, and [BFA], respectively, were varied, holding the other reagents constant. The results show that equation (15) is generally valid for the system. It is not possible to determine k_0 accurately, as the average extinction coefficient of the chromophores is not known, but it is of the order of 2 to 6 $(\mathrm{l.\ mole}^{-1})^{\frac{3}{2}}$ $\mathrm{min.}^{-1}$.

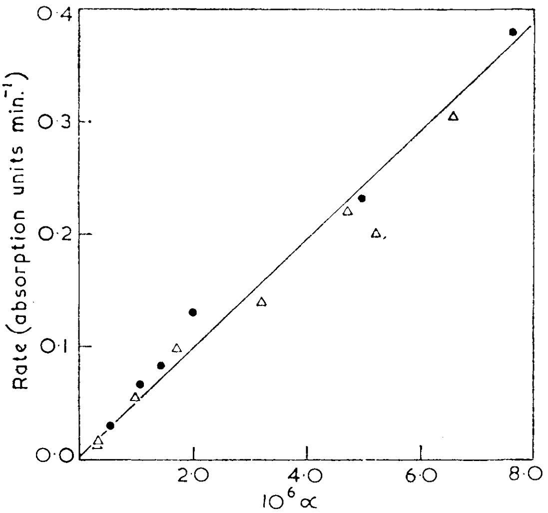

FIG. 4. Reactions in varying catalyst conditions.

Initial olefin = cis-But-2-ene, 0·50 mole $\mathrm{l.}^{-1}$; △ [BFA] varied with $[\mathrm{BF}_3]_{\mathrm{soln.}} = 2{\cdot}5 \times 10^{-3}$ mole $\mathrm{l.}^{-1}$; ● [BFA] = $2{\cdot}0 \times 10^{-2}$ mole $\mathrm{l.}^{-1}$ with $[\mathrm{BF}_3]_{\mathrm{soln.}}$ varied.

Some attempts were made to correlate the rate and [polymer] increments in the induction periods of the reactions but the results proved too erratic to be useful.

To summarise: There is no indication of the formation of spectra due to alkyl carbonium ions in the systems containing normal butenes, boron trifluoride, and a co-catalyst in ethylene dichloride. The kinetic results suggest the formation of aliphatic alkenyl ions by hydride transfer from olefins to the minute quantities of alkyl ions present in the systems. The spectra at 304 ± 2 mμ agree well with those obtained from compounds which might be expected to give alkenyl ions in similar systems. Isobutene may give a tertiary carbonium ion, but the spectrum has a peak at a wavelength (285 mμ) considerably lower than the absorption peaks formed in kinetic runs.

The author thanks Dr. A. M. Eastham for his interest and advice.

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NATIONAL RESEARCH COUNCIL, OTTAWA, CANADA. [*Received, February* 10*th*, 1964.]