Reactions of Ethylene with Triethyl Aluminum: Effect of Operating Variables and Kinetics of Reaction

LYLE F. ALBRIGHT and CLAYTON S. SMITH

Purdue University, Lafayette, Indiana

Trialkyl aluminums, frequently referred to as *Ziegler catalysts*, have within the last few years been used extensively in several processes involving olefin chemistry, including the production of higher α-olefins, high polymers, and fatty acids. Several articles reviewing the chemistry of trialkyl aluminum have been published (*6, 19* to *21*).

The most important reactions occurring between trialkyl aluminum and olefins such as ethylene are shown as follows:

$$al\text{—}R + CH_2{=}CH_2 \rightarrow al\text{—}CH_2\text{—}CH_2\text{—}R \quad \text{(growth reaction)} \quad (1)$$

$$al\text{—}CH_2\text{—}CH_2\text{—}R' + CH_2{=}CH_2 \rightarrow al\text{—}CH_2\text{—}CH_3 + CH_2{=}CH\text{—}R' \quad \text{(displacement reaction)} \quad (2)$$

where $al = Al/3$

Furthermore, trialkyl aluminums decompose to form hydrides:

$$al\text{—}CH_2\text{—}CH_2\text{—}R' \rightarrow al - H + CH_2{=}CH\text{—}R' \quad (3)$$

The hydrides react with an olefin such ethylene as follows:

$$al\text{—}H + CH_2{=}CH_2 \rightarrow al\text{—}CH_2\text{—}CH_3 \quad (4)$$

Possibly the displacement reaction (2) is actually a combination of (3) and (4). In general, most commercial interest for these reactions occurs at temperature from about 100° to 220°C. Decomposition becomes a problem above about 200°C.

The mechanism of the reactions has been considered by several investigators. Ziegler (*22*) and Skinner et al. (*13*) both report that the distribution of alkyl groups produced follows a Poisson type of distribution with possibly a slight tendency to favor the higher molecular weight products. Ziegler has indicated without presenting experimental data that the rates of the growth reactions are directly proportional to the ethylene concentration (*18, 21*) and to the square root of the concentration of the trialkyl aluminum (*18*). Ziegler considers this latter finding as evidence that the monomeric form AlR_3 of the catalyst is the active species rather than the dimeric form Al_2R_6. Natta (*12*), however, found that the rate was directly proportional to the concentrations of both ethylene and trialkyl aluminum.

Although considerable commercial interest is being shown in the production of higher olefins (*1, 3, 5, 6, 10, 11*), more information is still needed on ways for optimizing the yields of the desired products and on the mechanism of the reactions. The addition of extremely small amounts of nickel salts to the reaction mixture promotes displacement reactions relative to growth steps (*2, 9, 18, 23*), but the role of the nickel is not known. Transfer of the olefins to the liquid phase containing the trialkyl aluminum is obviously important in the process. In order to clarify the reactions and in order to obtain kinetic information, extensive data have been obtained for the reactions between triethyl aluminum (TEA) and ethylene. A mechanism is postulated in part based on the kinetic results.

EQUIPMENT AND OPERATING PROCEDURE

The stirred-tank reactor used in this investigation was a 300 cc. capacity autoclave purchased from Autoclave Engineers. It had an internal diameter of 1 13/16 in., inside height of 7 in., and was constructed from 316 type stainless steel. The Dispersomax turbine impeller was generally operated at 875 rev./min. The reactor was provided with a liquid sampling line, a vent line with an attached partial condenser, a pressure gauge and an extra line to the condenser so that the liquid formed in the condenser could be easily drained back to the reactor. The reactor was provided with electrical heaters.

Solutions of triethyl aluminum (TEA) were transferred to the reactor with high-purity dry nitrogen. Two solutions of approximately 10% by weight TEA were obtained premixed from Texas Alkyls. The solvents in these solutions were Varsol or technical grade *n*-decane. The Esso Research and Engineering Company reported that the relatively high boiling Varsol contained 31% aromatics, 21% naphthenes, 35% paraffins, and 13% condensed napthenes.

Chemically pure ethylene obtained from the Matheson Company was first dried with a P_2O_5 tube, was metered with a sharp edged orifice, and entered the reactor through a dip tube. The bottom of the dip tube was located near the bottom of the reactor below the liquid level. The gases from the reactor usually exhausted through an air cooled condenser plus a heated line containing a back pressure regulator. The exhaust gases could be metered with a soap-bubble flowmeter or could be analyzed for all major components with a two-column gas chromatrographic unit. One column was used for all hydrocarbons up to C_6's and the other for heavier hydrocarbons. The unit was calibrated so that the analyses were in general accurate to within 5% or less.

After the reactor was loaded with 150 cc. of solution containing TEA, hydrocarbon solvent, and nickel salts, the reactor was pressured with ethylene. Special care was taken so that no air or moisture entered the system. The agitator was started, the reactor was heated to the run temperature, and the pressure was adjusted with the back pressure regulator. When the desired temperature was obtained, the ethylene flow

---

Clayton S. Smith is with the Morton International Research Laboratory, Woodstock, Illinois.

was started. Approximately 0.5 to 1.0 hr. were required to start up the system and to obtain temperature control within 0.2°C. flow rates within 1 to 2%, and changes of pressure normally less than 0.1 lb./sq. in. During the course of the run, the flow rate and analyses of the exhaust gases were determined several times. Liquid samples were also taken during each run. These samples were hydrolyzed, and the resulting paraffin gases were analyzed with a gas chromatographic column.

RESULTS

A total of 104 runs were made over the following ranges of operating variables:

Temperature,	80° to 220°C.
Pressure,	15 to 135 lb./sq.in.abs.
Concentration of TEA in starting solution,	1 to 10% by weight
Nickel (as salt) added,	0.0 to 0.6 g.
Agitation,	850 rev./min.

Product Analysis

Butenes, especially 1-butene, were the major gaseous products of all runs of this investigation. When fresh nickel salts were added at relatively low temperatures (as will be discussed later), 2-butenes were initially the major products, and they were apparently formed by isomerization of 1-butene. Often the cis to trans ratio of 2-butene was about 1 to 2, indicating essentially thermodynamic equilibrium. The production of 2-ethyl-1-butene generally decreased when the production of 1-butene decreased. Reaction of 1-butene with ethyl-aluminum groups would be a likely mechanism for the production of 2-ethyl-1-butene. The amounts of hexenes, including 1-hexene, tended to decrease as a run proceeded. 2-ethyl-1-hexene was the major octene detected, but generally few, if any, octenes were noted in the off gases. Octene concentrations might have increased if the runs had been continued for long periods of time. Traces of propylene, isobutane, propane, and perhaps methane were generally observed in the gas stream. Several peaks, including some which were apparently C_5 olefins, were detected in the initial stages of most runs with fresh catalyst. Possibly a few propylaluminum groups were present in the fresh catalyst. One component which is probably either 3- or 4-methyl-1-pentene occurred in trace quantities during the entire course of several runs.

In all cases, only part of the ethylene reacted, and it was always the major component in the exhaust gas stream. Material balances based on the analyses and on the flow rates of the entering and exhaust gas streams indicated that in general a relatively small fraction of the ethylene was retained in the reactor for most runs. The ethylene could have been retained as either dissolved ethylene, dissolved reaction products, or reaction products between ethylene and TEA.

Deactivation of the Catalyst

The activity of the catalyst decreased significantly during the course of several runs. Such a decrease could be caused either by the buildup of less reactive alkyl groups on the catalyst, by irreversible types of decomposition, or by actual destruction of the catalyst by impurities such as moisture, acetylenes, etc. Treatment of the entering ethylene with a separate TEA solution in addition to P_2O_5 did not reduce the loss of catalyst activity, so this treatment was discontinued. The loss of activity was apparently caused mainly by the first two factors mentioned above.

In a run at 100°C., the fraction of feed ethylene that reacted and was exhausted as higher olefins in the exit gas stream increased with time from 13 to 17%. Approximately 8 to 10% of the ethylene was not accounted for based on a material balance. Immediately following this run, another run was made at 140°C. with the same catalyst solution. In the first stages of this run, 16% of the ethylene remained in the liquid phase and 45% of the ethylene reacted. After 2 hr. of the run, the values had become 11 and 32 to 35%, respectively.

Runs made at a low catalyst concentration (1% TEA) reached an apparent steady state value after several hours, but 10 to 15% of the ethylene was retained, indicating that the catalyst was being diluted.

Effect of Agitation

The normal level of agitation, namely 850 rev./min., was sufficient to eliminate most of the mass transfer resistances between the gas and liquid phases in the reactor. This conclusion is based on two types of experimental information. First, runs made at both 850 and 1,700 rev./min. indicated no differences in the type or rate of reaction even at high rates of reaction.

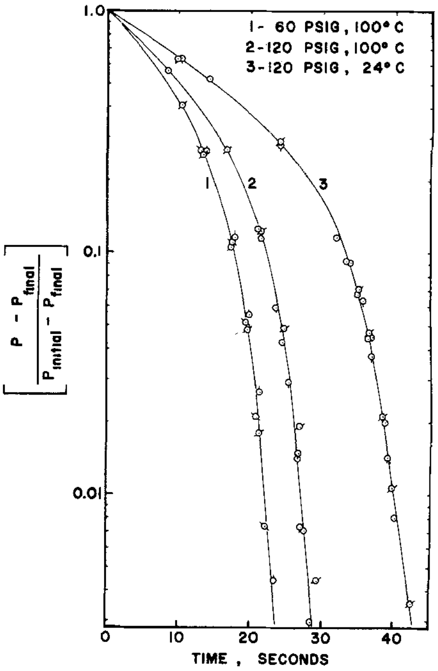

Fig. 1. Determination of mass transfer coefficients.

Second, calculations based on mass transfer coefficients (K_TA) also indicated that the ethylene concentrations in the liquid phase during a run were 98% or more of the equilibrium concentrations. These mass transfer coefficients were determined experimentally for ethylene at 850 rev./min. and at pressures from 25 to 120 lb./sq.in.gauge. In these measurements, the solvent was first added to the autoclave, and then the gas portion of the autoclave was filled with ethylene. The agitator was started, and the pressure drop caused by ethylene absorption was followed for several runs as a function of time. The rate of ethylene absorption is given as follows:

$$\text{Rate of absorption} = K_TA \ (P - P^*)$$

When one assumes an ideal gas and Henry's law, the equation can be integrated as follows:

$$\log \frac{P - P_f}{P_i - P_f} = - \frac{K_TA}{2.303} \left[\frac{1}{V_L K_E} + \frac{RT}{V_G} \right] t \quad (5)$$

The experimental data for several runs were plotted from Equation (5), as shown in Figure 1. Solubility data had also to be determined experimentally in some cases as will be discussed later. K_TA values were calculated based on the slopes after 20 sec. of each run. The first portion of the run was required to develop a fine, uniform, gas-liquid dispersion and to develop the maximum transfer coefficients. K_TA values of 0.122, 0.126, 0.143, and 0.124 m.-moles/sec., lb./sq.in. were determined for these runs. Presumably the mass transfer coefficients during the reaction runs were similar to these values.

Solvent Effects

Comparable runs made with the two solutions of TEA as catalyst (that is, one having *n*-decane as solvent and the other Varsol) indicated no significant differences relative to the course or rate of reaction.

Pressure Effect

The effect of pressure on the reactions was determined in each of two series of runs. One series was made at 152°C. with 10% TEA in *n*-decane. The other series was also made at 130°C. with 10% TEA in *n*-decane, but 5 g. of 6% nickel naphthenate was also added. The ethylene flows were regulated during the runs in order to maintain essentially constant mole fractions of ethylene in the gas phase. The ethylene partial pressure was assumed to be equal to the mole fraction of ethylene in the product gas multiplied by the difference between the absolute pressure of the reactor and the vapor pressure of *n*-decane. The method is not perfect, since some heavier components and solvents are being refluxed, but it should be reasonably accurate. At 0 and 30 lb./sq.in.gauge, there was no significant catalyst deactivation, but some occurred at 75 and 120 lb./sq.in.gauge. Data at the higher pressures were extrapolated by a straight-line method back to the start of the run at 75 lb./sq.in.gauge. Figure 2 indicates that the rate of ethylene reaction was directly proportional within experimental accuracy to the partial pressure of ethylene for both series of runs.

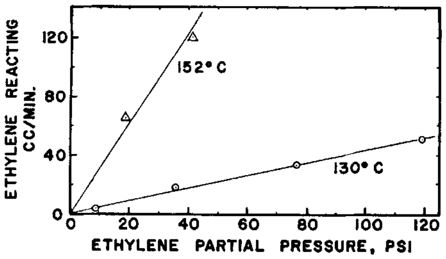

Fig. 2. Effect of pressure on rate of reaction.

Effect of Temperature and TEA Concentration

Data above 180°C. were unreliable because of extensive refluxing of both the products and the solvent. Since the reaction depends on the amount of dissolved ethylene, the effect of temperature on solubility had to be considered in calculating the fraction of the dissolved ethylene, reacting per minute.

$$\frac{\text{Fraction reacting}}{\text{min.}} = \frac{\text{mole of ethylene reacted}}{(\text{min.}),(\text{mole of ethylene dissolved})} = \text{Rate}_2 \quad (6)$$

The fraction reacting per minute was determined for thirty-three runs as a function of both TEA concentration and temperature. Figure 3 shows the results for series of runs at 30 lb./sq.in.gauge and at a constant ratio of nickel naphthenate to TEA. In most cases, the material balances for these runs were good. At 180°C., the fraction reacting was linearly dependent on the catalyst concentration but was more complicated at both 140° and 160°C. The results at 100° and 120°C. are less definitive because the reaction rates were low, and relative experimental inaccuracies became significant.

Several additional runs without nickel catalyst showed similar dependence on temperature and catalyst concentration.

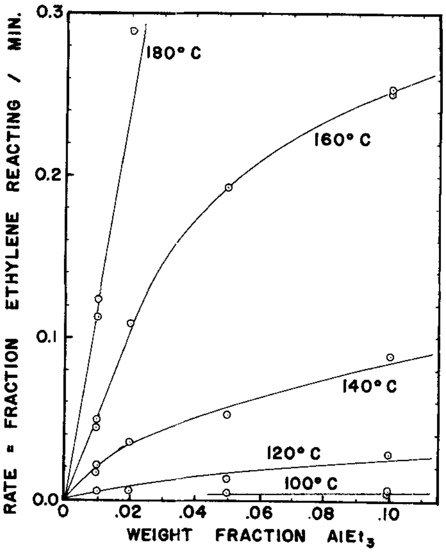

Fig. 3. Effects of temperature and concentration of TEA on rates of reaction.

Nickel Effects

Both 6% nickel naphthenate in mineral oil [recommended by Continental Oil Company (*2*)] or nickel acetylacetonate (used by Ziegler) were used in numerous runs. Phenyl acetylene was added in several runs as recommended by Ziegler (*18*). During the first several hours after nickel was added to the reactor, up to 70% of the butenes were cis or trans 2-butenes. With time, this fraction decreased, and 1-butene became the primary product. The decrease was more rapid at high temperatures. One run made at 80°C. indicated that most of the butenes were still 2-butenes after several hours of operation. Based on the formation of 1-hexene, the displacement reaction was not significantly increased by the nickel. Possibly such an effect could have occurred early in the run and was unobserved.

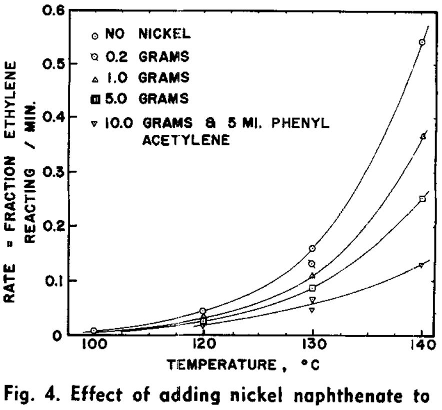

Fig. 4. Effect of adding nickel naphthenate to to 10% TEA.

The addition of the nickel decreased the rate of ethylene reacting, as shown in Figure 4. The addition of 1.0 g. of nickel naphthenate solution to 150 ml. of 10% TEA in *n*-decane reduced the rate of the ethylene reaction by about 30% between 100° and 160°C. Further nickel addition had less additional effect on the rate.

When runs with nickel acetylacetonate and nickel naphthenate were compared at similar molar concentrations of nickel, the rates of reaction were essentially identical. Nickel or nickel salts slowly precipitated out of the solution to form black deposits which were found when the reactor was opened after a number of runs.

Solubilities of Olefins in the Liquid Phase

The solubilities of ethylene and 1-butene were determined experimentally in the pure solvents at various pressures and temperatures. The autoclave was partially filled with the desired solvent, and the olefin was then added. Equilibrium was obtained after several minutes of agitation; the pressure and temperature of the system were recorded. The olefin was slowly vented, while vigorous agitation was provided until atmospheric pressure was reached; the amount of olefin vented was measured. When we know the equilibrium pressure and temperature, atmospheric pressure and temperature, liquid volume, gas volume in the autoclave, and the volume of gas exhausted, we can calculate the amount of olefin dissolved in the solvent above the amount dissolved at atmospheric pressure. Henry's law was found to apply, and the amount at atmospheric pressure was determined by extrapolation. The gas solubilities were essentially identical in both pure solvents as well as in the 10% solutions of TEA. The solubility constants, expressed as mole per pound per square inch absolute, liter solvent are represented by the following equations from 28° to 160°C:

$$K_E = 2.91\ (10^{-4})\ \exp\ (997.5/T) \tag{7}$$

$$K_{1-B} = 0.917\ (10^{-4})\ \exp\ (2{,}171.1/T) \tag{8}$$

Solubility constants for other C_4 and C_6 olefins were estimated from the generalized tables of Hadden (*8*) and Winn (*17*).

KINETICS OF REACTION

Evaluation of the kinetic data for this gas-liquid system is complicated by several factors, including catalyst deactivation and the need to operate the system for several hours to obtain essentially steady state operation. Fortunately, deactivation, especially at lower pressures and lower catalyst concentrations, was low. The kinetic data were corrected to constant catalyst activity by extrapolation to values for catalysts that had been used 4 hr. Such catalysts were assumed to have essentially reached steady state conditions relative to dissolved hydrocarbons and relative to alkyl groups attached to the aluminum atom.

Temperature affected not only the basic reaction but also the solubility of ethylene in the liquid phase and the following association reaction of the trialkyl aluminum, shown here as TEA:

$$2\ \mathrm{AlEt_3} \rightleftharpoons \mathrm{Al_2Et_6} \tag{9}$$

The equilibrium constant for Equation (9) is as follows:

$$K_a = \frac{(\mathrm{Al_2Et_6})}{(\mathrm{AlEt_3})^2} \tag{10}$$

If C represents the mole fraction of $\mathrm{AlEt_3}$ which would be present with the assumption of complete dissociation of $\mathrm{Al_2Et_6}$, then

$$2(\mathrm{Al_2Et_6}) + (\mathrm{AlEt_3}) = C \tag{11}$$

The actual mole fraction of $\mathrm{AlEt_3}$ monomer at equilibrium conditions in the system is calculated as

$$(\mathrm{AlEt_3}) = \frac{-1 + (1 + 8\ K_aC)^{0.5}}{4\ K_a} \tag{12}$$

and the concentration is given as follows:

$$[\mathrm{AlEt_3}]_{\mathrm{Monomer}} = D(\mathrm{AlEt_3}) \tag{13}$$

By assuming that the mole fraction of the monomeric form of triethyl aluminum is given by Equation (12), and by using the solubility of ethylene in the reaction media described by Equation (7), the experimental data were tested by using the following rate expression:

$$\mathrm{Rate_1} = k\ [\mathrm{C_2H_4}]\ [\mathrm{AlEt_3}]_{\mathrm{Monomer}} = \frac{\text{moles ethylene reacting}}{\text{min., liter}} \tag{14}$$

Rate data taken at 130° and 152°C., constant TEA concentrations, and partial pressures of ethylene from 9 to 120 lb./sq.in. were plotted in Figure 2. Since the rate is directly proportional to the ethylene concentration, the following simplification of Equation (14) is then possible:

$$\mathrm{Rate_2} = \frac{\mathrm{Rate_1}}{[\mathrm{C_2H_4}]} = k[\mathrm{AlEt_3}]_{\mathrm{Monomer}} = \frac{\text{moles ethylene reacting}}{\text{min., mole ethylene dissolved}} \tag{15}$$

Values of K_a were calculated from the kinetic data (*14*) and the assumption that Equation (15) is applicable. Table 1 presents the values obtained based on these kinetic data. Values of the dissociation constant K_D ($K_D = 1/K_a$) have recently been determined by thermochemical means (*15*), and K_a values by this latter method are also shown in Table 1. The agreement between the kinetic and thermochemical values of K_a was rather good, when we consider the indirectness and uncertainties of the kinetic approach. These equilibrium values were used to estimate the heat of dissociation of TEA as about 20 kcal./g.-mole, which is similar to 20.2 kcal./g. mole for trimethyl aluminum reported earlier (*4*).

TABLE 1. COMPARISON OF K_a VALUES

Temp., °C	K_a Kinetic	K_a Thermochemical
120	167	239
140	48	83
160	16	32

An attempt was made without success to modify the kinetic equations presented above and to include a term to represent the nickel added to the system. Kinetic data obtained both with and without nickel in the system were correlated, however, from the above equations.

The values of K_a based on thermochemical measurements (*15*) were employed to calculate the TEA monomer concentration. Figure 5 is a plot of the rate ($\mathrm{Rate_2}$) vs. the concentration of monomeric TEA in the reaction mixture. A relatively good fit of the kinetic data at each temperature was obtained by this method. Individual data points for 100°, 120°, and 130°C. are not shown on

Figure 5 in order to preserve clarity. The slope of the best straight lines for each set of data at a given temperature is equal to the rate constant k. These k values have been correlated from an Arrhenius type of plot (Figure 6). The activation energy for the reaction was calculated as being 15 kcal./mole.

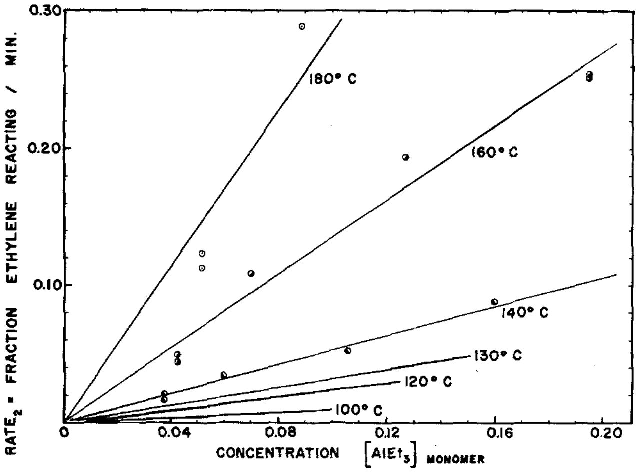

Fig. 5. Determination of reaction rate constants.

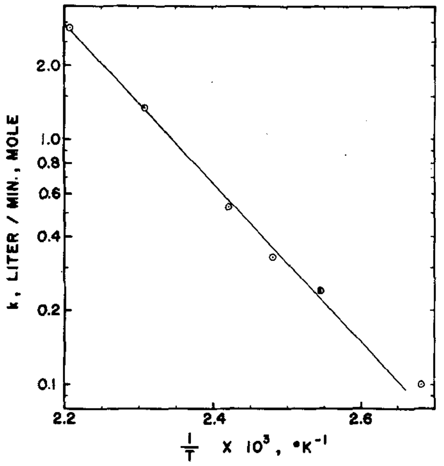

Fig. 6. Arrhenius type of plot of reaction rate constant.

Use of Equation (14) involves several assumptions:

1. The solubility of ethylene in the liquid phase of the reactor is the same as that of the pure solvent. The composition and quantity of the liquid phase are obviously somewhat different than those of the starting catalyst solution. The basic assumption is probably reasonably good.
2. The dissociation of the trialkyl aluminums in the reactor to the monomeric form AlR_3 is the same as that of TEA. Some relatively large alkyl groups R are, of course, attached to the aluminum atom. As the alkyl groups become larger, dissociation of the trialkyl aluminum increases. As a result, calculated values for the abscissa of Figure 5 may be somewhat low. The volume of the liquid phase increases, however, as hydrocarbons are dissolved, which to some extent at least counterbalances the above factor.
3. No appreciable destruction of the catalyst occurred at the end of 4 hr. This was the time to which the experimental data were extrapolated to obtain a constant catalyst activity.

Based on the kinetic model, the rate controlling step is the reaction(s) of dissolved ethylene with trialkyl aluminum catalyst, that is, Equations (1) and (2). Furthermore, the monomeric form of the trialkyl aluminum is the active catalyst and not the dimer. At high concentrations of TEA, additional solubility data would be required, since the present data would likely not be applicable.

ALKYL GROUP DISTRIBUTION IN LIQUID

A number of chemical models were assumed, and analytical expressions for each were developed and solved on an IBM digital computer (*14*). The computer results were compared to available experimental data, especially those of Ziegler (*22*). A series of equations for transient conditions were derived based on 0.5, 1.0, 1.5, and 2.0 order reactions relative to the active catalyst. Initially the ratio constants for the various reaction steps were assumed to be independent of the length of the alkyl group attached to the aluminum atom. The first-order equations gave the best fits, except the experimental data indicate more of the heavier alkyl groups. If the rate constants were somewhat higher for the smaller alkyl groups, the analytical models would do a somewhat better job of predicting the distribution of the alkyl groups.

Weslau (*16*) has discussed the approximate solution of equations in which the growth rate was about thirty times larger than the displacement rate. Friedman and White (*7*) have partially solved equations of such a model. Since the present investigation indicates that steady state conditions were only approximated, there is a need to develop additional models that consider the solutions for the unsteady state competing growth and displacement reactions of the alkyl groups in the liquid phase. Such equations have now been derived and solved (*14*), but sufficient experimental data are not yet available to test them completely. Reliable data will be required in which the alkyl groups vary over a wide range of molecular weights.

The catalyst liquid phase in the reactor was analyzed in several cases by hydrolysis followed by analysis of the paraffins formed. The results are sufficient to give a rough comparison of the displacement and growth rate constants:

$$\text{Rate of growth of } n^{\text{th}} \text{ chain} = k_n\,(C_2H_4)\,(X_n)$$
$$\text{Rate of displacement of } n^{\text{th}} \text{ chain} = k_n'\,(X_n)$$

At steady state conditions

$$\frac{dx_{n+1}}{dt} = k_n(C_2H_4)\,(X_n) - k_{n+1}(C_2H_4)\,(X_{n+1}) - k'_{n+1}\,(X_{n+1}) = 0 \quad (14)$$

So

$$\frac{X_n}{X_{n+1}} = \frac{k_{n+1}}{k_n} + \frac{k'_{n+1}}{k_n(C_2H_4)} \quad (15)$$

Figure 7 indicates experimental values of X_n/X_{n+1} plotted vs. the reciprocal of the dissolved concentration of ethylene (C_2H_4) for three consecutive runs. The ratios of C_2/C_4 and C_4/C_6 alkyl groups are each represented reasonably well by a single straight line. At the highest value of $1/(C_2H_4)$, that is, 7.7, the points shown are considered less reliable since they represent the first run of the series, and possibly steady state conditions had not yet been obtained. Only trace quantities of C_8's were detected in the analyses of the liquid.

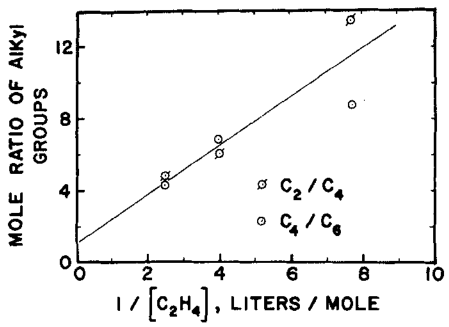

Fig. 7. Effect of dissolved ethylene on alkyl distribution.

Based on theory, if the intercept of Figure 7 was 1.0 (that is $k_{n+1}/k_n = 1$), the addition rates would be independent of the chain length. The data are not sufficiently accurate to make a definite conclusion on this point, but an intercept of 1.0 approximates the data reasonably well. The slope of the straight line indicates that k'_{n+1}/k_{n+1} equals 1.36. Calculation of k_{n+1} at 152°C. gives 0.8 ml./min., m.-mole; hence, k'_{n+1} equals 1.1 min.^{-1}.

If k'_{n+1} equals 1.1 min.^{-1}, then the decomposition half-life of an aluminum-butyl group is approximately 1 min. Such a time is significantly lower than values reported by Ziegler (*24*). Additional information is needed to explain this difference, and Smith (*14*) has discussed several possible reasons.

CONCLUSIONS

The reactions between triethyl aluminum and ethylene have been investigated over a wide range of operating conditions. Kinetic data were obtained for runs in which at least 95% of the mass transfer resistances were eliminated. The reaction is first order with respect to the concentration of the dissolved ethylene in the liquid and with respect to the monomer of triethyl aluminum. Under the conditions studied, nickel salts did not promote the formation of low molecular weight olefins as previously reported, but they did decrease the rates of reaction probably by destruction of triethyl aluminum. Rate constants for both the growth and displacement reactions have been approximated.

ACKNOWLEDGMENT

The American Cyanamid Company, Procter and Gamble Company, and Union Carbdie provided generous financial assistance. Dr. R. E. Hall of Procter and Gamble and Drs. M. T. Atwood and P. A. Lobo of Continental Oil offered valuable suggestions during the investigation. Continental Oil purchased the solutions of aluminum triethyl, and Esso Research and Engineering Company provided Varsol solvent.

NOTATION

$(AlEt_3)$ = mole fraction of the monomer of triethyl aluminum (TEA)
(Al_2Et_6) = mole fraction of the dimer of TEA
$[AlEt_3]$ = mole concentration of the monomer of TEA, moles/liter of liquid
C = mole fraction of TEA if completely dissociated to $AlEt_3$
$[C_2H_4]$ = mole concentration of ethylene in the liquid phase, mole/liter
D = mole density of reaction media, moles/liter
k = forward rate constant for growth reaction
k' = forward rate constant for displacement reaction
K_a = equilibrium constant for association of TEA dimer
K_E = solubility constant for ethylene in liquid phase, moles/lb./sq.in.abs., liter solvent
K_{1-B} = solubility constant for 1-butene in liquid phase, moles/lb./sq.in.abs., liter solvent
K_TA = mass transfer coefficient between gas and liquid phases
P = reactor pressure, lb./sq.in.abs.
P_f = final reactor pressure, lb./sq.in.abs.
P_i = initial reactor pressure, lb./sq.in.abs.
P^* = equilibrium pressure in lb./sq.in.abs. of gas dissolved in liquid phase
Rate_1 = moles ethylene reacting/liter, min.
Rate_2 = moles ethylene reacting/moles ethylene dissolved, min.
R = gas constant
T = absolute temperature, °K.
t = time
V_G = volume of gas phase in reactor
V_L = volume of liquid phase in reactor
X = mole concentration of alkyl group and subscript refers to ethylene groups incorporated into alkyl group

LITERATURE CITED

1. Acciarri, J. A., W. B., Carter, and F. Kennedy, *Chem. Eng. Progr.*, **58**, No. 6, 85 (1962).
2. Atwood, M. T., Continental Oil Co., Poca City, Okla., private communication (1961).
3. *Chem. Week*, 73 (May 6, 1961).
4. Coates, G. E., "Organo-Metallic Compounds," p. 130, Wiley, New York (1960).
5. Ethyl Corp. (by T. H. Pearson and J. K. Presswood), *Brit. 990, 748* (Apr. 28, 1965).
6. Fel'dblym, V. Sh., L. D. Myasuikova, A. M. Eut'in, S. I. Kryukov, and M. I. Farberov, *Internat. Chem. Eng.* **6**, No. 2, 276 (1966).
7. Friedman, M. H., and R. R. White, *AIChE J.*, **8**, 581 (1962).
8. Hadden, S. T., *Chem. Eng. Progr. Symposium Ser. No. 7* **49**, 53 (1953).
9. Lucas, G., Paper presented 142nd National Meeting of American Chemical Society, Atlantic City, N.J. (Sept., 1962).
10. "Montecatini Societa," pp. 586, 452, Generale per l'Industria Mineraria e Chimica, Italy (Oct. 22, 1957).
11. Techklenburg, H., and A. Kessler *Adv. Chem. Ser.* **34**, 145 (1962).
12. Natta, G. Symposium de Chimie Macromoleculaire de Milan-Turin (1954).
13. Skinner, W. A., E. Bishop, P. Camour, S. Fuqua, and P. Lim, *Ind. Eng. Chem.*, **52**, 595 (1960).
14. Smith, C. S., Ph.D. thesis, Purdue Univ., Lafayette, Ind. (1963).
15. Smith, M. B., *J. Phys. Chem.*, **71**, No. 2, 364 (1967).
16. Weaslau, H., *Ann.*, **629**, 198 (1960).
17. Winn, F. W., *Chem. Eng. Progr. Symposium Ser. No. 2* **48**, 121 (1952).
18. Zeiss, J., "Organometallic Chemistry," pp 194-269, American Chem. Soc. Monograph No. 147, Reinhold, New York (1960).
19. Ziegler, K., "Compete-rendu du XXXIe Congress Internationale de Chimie Industrielle, Liege (1959).
20. ———, "Perspectives in Organic Chemistry," p. 185, Interscience, New York (1956).
21. ———, H. G. Gellert, H. Lamkuhl, W. Pfohl, and K. Zosel, *Ann.*, **629**, 1 (1960).
22. Ziegler, K., H. G. Gellert, K. Zosel, E. Holzkamp, J. Schneider, M. Soll, and W. R. Kroll, *ibid.*, 127.
23. Ziegler, K., E. Holzkamp, H. Breil, and H. Martin, *Angew. Chem.*, **67**, 543 (1955).
24. Ziegler, K., W. R. Kroll, W. Larbig, and O. W. Stendel, *Ann.*, **629**, 53 (1960).

Manuscript received January 24, 1967; revision received July 21, 1967; paper accepted July 26, 1967. Paper presented at AIChE Houston meeting.