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Kinetics of Ethylene Polymerization and Butadiene Polymerization Catalyzed by Solutions of Hydridochlorotris(triphenylphosphine)ruthenium(II)

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The kinetics of ethylene polymerization and butadiene polymerization, catalyzed homogeneously by solutions of $HRuCl(PPh_3)_3$ in *N,N*-dimethylacetamide at 50-85°C, are reported. The reaction rates are first order in catalyst, and are first order in substrate for the ethylene system, but are independent of the substrate concentration in the diene system. The data are interpreted in terms of a common mechanism analogous to that of Ziegler catalysts, where, following coordination of the monomer to metal, the polymer chain grows by insertion of the monomer at a polarized metal-carbon bond. The differences in kinetics are accounted for by the stronger complexing ability of the diene. The activation parameters obtained show that the butadiene polymerization rate is higher because of a more favorable entropy of activation. The catalyst becomes deactivated due to decarbonylation of the solvent, and possibly due to an intramolecular hydrogen transfer process involving a phenyl ring of the phosphine ligand.

INTRODUCTION

During the last few years, extensive work has been carried out on oligomerization and polymerization reactions of olefins using transition metal complexes as homogeneous catalysts (*1-3*). As in the case of Ziegler-Natta catalysts, the olefin is thought to coordinate to a vacant site on the metal ion to which is attached the growing polymer chain R; an insertion reaction then occurs by a rate-determining migration of the group R(4). In general, most studies have naturally been concerned with product composition, and little kinetic data have been reported for the homogeneous reactions (*3*), although Cramer's detailed kinetic and mechanistic study on the dimerization of ethylene catalyzed by rhodium trichloride may be considered a classic in this area (*5*); this system and others involving salts of the Group VIII metals involves initiation via a metal hydride.

During some studies on homogeneous hydrogenation using the well-known catalyst hydridochlorotris(triphenylphosphine) ruthenium(II) [$HRuCl(PPh_3)_3$] under mild conditions (*6, 7*), we observed continuous uptake of both ethylene and butadiene by *N,N*-dimethylacetamide (DMA) solutions of this complex in the absence of hydrogen. This paper reports some preliminary data, particularly on the kinetic aspects of these polymerization reactions.

Polymerization reactions catalyzed homogeneously by ruthenium complexes have been reviewed recently (*7*).

EXPERIMENTAL

Materials. Ruthenium was obtained as the trihydrate $RuCl_3 \cdot 3H_2O$ from Johnson Matthey Co. All gases were obtained from Matheson Co. Ethylene and butadiene were CP grade (99.5 and 99.0%, respectively). For some experiments, the ethylene was purified by freezing to liquid nitrogen temperatures followed by pumping to remove the noncondensible gases. Butadiene and vinyl fluoride were purified for all experiments by the same procedure. Prepurified hydrogen (99.95%) was passed through a Deoxo catalytic purifier to remove traces of oxygen before use. Lithium chloride (Allied Chemical) and triphenylphosphine (Strem Chemicals) were reagent grade; the latter was recrystallized before use. Certified DMA (Fisher Scientific Co.) was distilled under nitrogen from calcium hydride, and was stored under nitrogen on Linde 5A molecular sieve.

Catalyst preparation. The dichloro complex $RuCl_2(PPh_3)_3$ was prepared according to the method of Stephenson and Wilkinson (*8*). We have noted earlier (*9*) that $HRuCl(PPh_3)_3$ can be prepared *in situ* in DMA by reaction of hydrogen with the dichloro complex; we now find that the DMA solvate $HRuCl(PPh_3)_3 \cdot DMA$ can be readily isolated from more concentrated solutions, the procedure being more convenient than that for preparation of the corresponding benzene solvate (*6*):

$$RuCl_2(PPh_3)_3 + H_2 \rightarrow HRuCl(PPh_3)_3 + H^+ + Cl^-. \quad (1)$$

About 0.5 g of the dichloro complex was added to 5 ml DMA under vacuum; the brown suspension was then shaken under hydrogen (up to 1 atm) with gentle warming. On standing overnight, dark violet crystals of the hydride precipitated; these were collected, washed quickly with DMA and stored *in vacuo*. Excess solvent was removed by pumping (50% yield). Calculated for $RuClP_3C_{58}H_{55}NO$: C, 68.9; H, 5.5; N, 1.4; Cl, 3.5. Found: C, 68.8; H, 5.5; N, 1.3; Cl, 3.7. The infrared spectrum (nujol) exhibited a ruthenium–hydride stretch at 2030 cm^{-1} and a carbonyl band at 1650 cm^{-1}. The small shift of the carbonyl peak from its position for DMA itself (1660 cm^{-1}) indicates that the DMA molecule is probably not coordinated, since this results in much larger shifts (*10*). The violet crystals darkened slowly on exposure to air; DMA solutions of the hydride were extremely air-sensitive and rapidly turned green, and then finally yellow-brown. The green solutions, which have an absorption maximum at 630 nm ($\epsilon = 1300$), contain triphenylphosphine oxide; a similar oxidation is observed in benzene solution (*6*). In contrast to a recent report (*11*), we find no evidence from O_2 uptake measurements for formation of a molecular oxygen complex at room temperature in either benzene or DMA media.

Conductivity measurements on DMA solutions of the hydride at room temperature indicated that there was no significant ionization of chloride; triphenylphosphine readily dissociates to give a solvated species (*6, 7*):

$$HRuCl(PPh_3)_3 \rightleftharpoons HRuCl(PPh_3)_2 + PPh_3. \quad (2)$$

Procedure. The procedure for kinetic studies involved measurement of olefin gas uptake at constant pressure essentially using the apparatus and method described previously (*12*). The catalyst was suspended in a glass bucket over the solvent (2 ml) during degassing and gas-filling procedures, and was added only after several minutes shaking of the reaction flask to ensure saturation of the DMA with gas at the required pressure and temperature. Using this technique, reproducible data were obtained when using the same catalyst and solvent batch. The uptake rates were usually recorded for about 1 hr. Reaction temperatures used were 50–85°C. The solubility of ethylene in DMA was $4.2 \times 10^{-2} M$ atm^{-1} and varied little with temperature from 70–85°C; Henry's Law was obeyed at least up to 1 atm pressure. The corresponding solubilities of butadiene and vinyl fluorine were greater, being 9.2×10^{-1} and $1.7 \times 10^{-1} M$ atm^{-1}, respectively at 80°C.

Infrared spectra were recorded using a Perkin Elmer 457 grating spectrophotometer. Infrared analysis of the polybutadiene microstructure was carried out in carbon disulphide solution using extinction coefficients calculated by Hampton (*13*) for vinyl and *cis*- and *trans*-vinylene linkages; the absorbances for the three linkages were measured at 911, 724, and 967 cm^{-1}, respectively. Visible absorption spectra were measured on a Perkin Elmer 202 spectrophotometer. In checking for reaction products, a Beckman GC2A gas chromatograph was used with Poropak Q, $AgNO_3$-triethyleneglycol, and dinonylphthalate columns.

RESULTS

Ethylene and butadiene were absorbed by DMA solutions of the hydride at conveniently measurable rates at 80°C using ca. 10^{-3}–10^{-2} M catalyst and up to 1 atm olefin pressure. No measurable uptake of vinyl fluoride occurred over a period of 3 hr at 80°C, at 10^{-2} M catalyst, and 1 atm pressure.

Ethylene Polymerization

Some gas uptake plots recorded for three different catalyst concentrations are shown in Fig. 1. The plots show an initial autocatalytic-type region (ca. 1000 sec) followed by a period of linear uptake which lasted for about 1 hr; the 'autocatalytic' region coincided with a color change of the solution from violet (λ_{max} 520 nm, ϵ = 1750) to amber (a continuum down to 350 nm, ϵ = 660 at 400 nm), which persisted throughout the linear region. A gradual decrease in the uptake rate was observed over several hours, and this was accompanied by a solution color change to yellow (a continuum down to 350 nm, with ϵ = 735 at 400 nm). The plots levelled off after an ethylene consumption of about 20 moles per mole of Ru (Fig. 2).

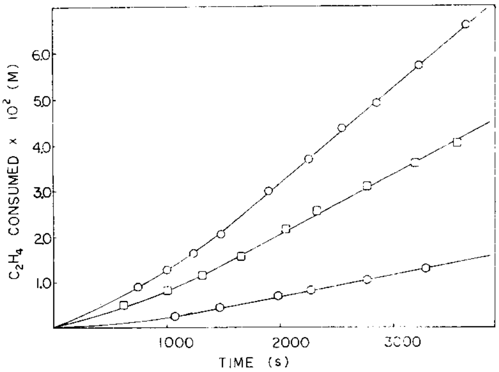


FIG. 1. Rate plots for ethylene uptake at 80°C, 725 mm C_2H_4. [Ru]: ⬡ 2.3×10^{-3} M; □ 4.5×10^{-3} M; ○ 9.8×10^{-3} M.

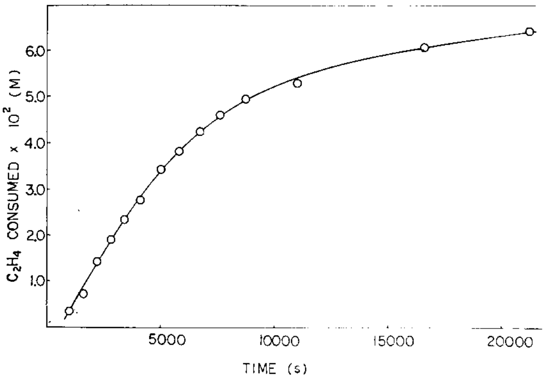


FIG. 2. Ethylene uptake plot at 80°; 725 mm C_2H_4, 3.1×10^{-3} M Ru.

The kinetics of the reaction were obtained from the linear region of the uptake plots (Table 1). The data show a good first-order dependence on ethylene up to a partial pressure (p') of 725 mm Hg (Fig. 3). The reaction is also first-order in catalyst up to the solubility limit of the catalyst (estimated to be 7×10^{-3} M); at higher concentrations, undissolved catalyst was observed in the solution after completion of the rate measurements. If CP grade ethylene were used without purification, the plot of rate vs catalyst concentration gave a positive intercept on the abscissa axis (Fig. 4, solid line). This effect is almost certainly due to destruction of some of the catalyst by oxygen impurity in the ethylene; purification of the ethylene resulted in increased rates (see Table 1) with the linear part of the ruthenium dependence plot now passing through the origin (Fig. 4, broken line) (ca.

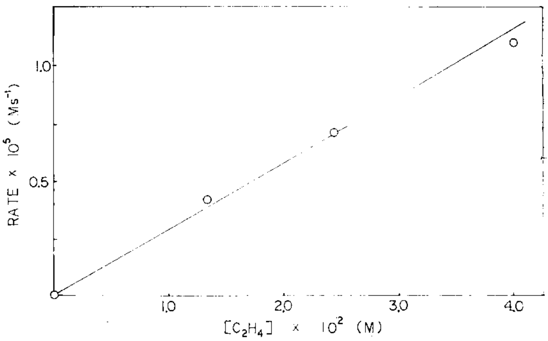


FIG. 3. Dependence of the linear rate on $[C_2H_4]$ at 80°C; 4.4×10^{-3} M Ru.

TABLE 1
SUMMARY OF RATE DATA[a]

Substrate	p' (mm)	10^2 [Catalyst] (M)	10^5 Rate (Ms^{-1})
C_2H_4	725	4.69	2.84
C_2H_4	725	1.49	2.33
C_2H_4	725	0.98	2.08
C_2H_4	725	0.45	1.31
C_2H_4	725	0.34	0.98
C_2H_4	725	0.29	0.76
C_2H_4	725	0.23	0.47
C_2H_4	725	0.17	0.24
C_2H_4[b]	725	0.18	0.63
C_2H_4[b]	725	0.23	0.89
C_2H_4[b]	725	0.34	1.12
C_2H_4[b]	725	0.34[c]	0.55
C_2H_4[b]	725	0.34[d]	0.34
C_2H_4	725	0.44	1.09
C_2H_4	441	0.44	0.71
C_2H_4	242	0.44	0.42
C_2H_4	375	0.44	0.28[e]
C_2H_4	735	0.44	0.50[e]
C_2H_4	725	3.31[f]	0.0
C_4H_6[b]	725	0.05	36.1[g]
C_4H_6[b]	725	0.05[f]	2.32
C_4H_6[b]	743	0.03	5.08[g,h]
C_4H_6[b]	743	0.07	14.9[g,h]
C_4H_6[b]	743	0.10	24.6[g,h]
C_4H_6[b]	743	0.05	9.06[g,h]
C_4H_6[b]	509	0.05	9.00[g h]
C_4H_6[b]	317	0.05	8.65[g,h]
C_4H_6[b]	166	0.05	8.57[g,h]
C_2H_3F[b]	725	0.45	0.0

[a] At 80°C, unless stated otherwise.

[b] Substrate purified.

[c] 0.61×10^{-2} M PPh_3 added.

[d] 3.4×10^{-2} M LiCl added.

[e] At 70°C.

[f] $RuCl_2(PPh_3)_3$ used instead of $HRuCl(PPh_3)_3 \cdot$DMA.

[g] Initial rate.

[h] At 65°C.

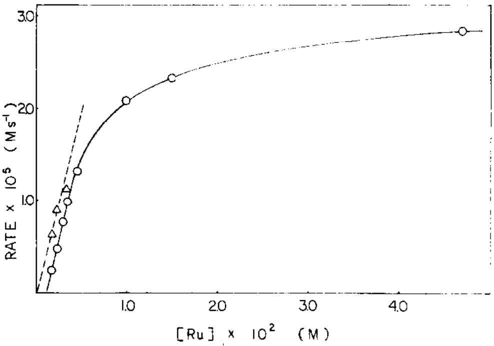


FIG. 4. Dependence of the linear rate on [Ru] at 80°C; 725 mm C_2H_4(—CP grade C_2H_4; --- purified C_2H_4).

0.1 M% oxygen impurity in the ethylene at 1 atm could account for oxidation of ca. 10^{-3} M of the catalyst in our system, which uses 2 ml solution and 50 ml gas volume). When using unpurified ethylene, solutions with low catalyst concentration have a greenish color which is evidence for partial oxidation of the catalyst; no green color was observed when using purified ethylene.

The rate can thus be written as $k_1[C_2H_4][Ru]$, where [Ru] is the total ruthenium concentration. Neglecting loss of some catalyst by reaction with oxygen impurity, Figs. 3 and 4 give the bimolecular rate constant at 80°C as 6.5×10^{-2} and 8×10^{-2} $M^{-1}s^{-1}$, respectively; allowing for the catalyst loss, the former value will be ca. 25% higher. Table 2 lists k_1 values determined at 70–85°C; the value at 80°C is somewhat lower than that estimated from Fig. 3, and this is attributed to use of a different batch of catalyst and purified DMA for the temperature variation experiments. The data give a good Arrhenius plot and the activation parameters $\Delta H^\ddagger = 20.0 \pm 0.7$ kcal mol^{-1} and $\Delta S^\ddagger = -7.7 \pm 2.0$ e.u.

Addition of about 2 moles of triphenylphosphine per mole of catalyst reduced the rate by about 2; addition of a tenfold excess of lithium chloride inhibited activity by a factor of 3.

TABLE 2
TEMPERATURE DEPENDENCE OF RATE CONSTANTS FOR POLYMERIZATION OF ETHYLENE (k_1)[a] AND BUTADIENE (k_2)[b]

Temperature (°C)	10^2 k_1 ($M^{-1}s^{-1}$)	Temperature (°C)	10^2 k_2 (s^{-1})
70	2.5	50	4.1
75	4.0	55	8.7
80	6.1	60	17.5
85	8.7	65	26.4

[a] [Ru] = 4.4×10^{-3} M, [C_2H_4] = 4.0×10^{-2} M.

[b] [Ru] = 5.0×10^{-4} M, [C_4H_6] = 1.0 M.

The decrease in rate at longer times (Fig. 2) is not due to a buildup of gaseous products with concomitant reduction in the partial pressure of ethylene, since evacuation and recharging the system with fresh ethylene did not increase the uptake rate.

No gaseous products were detected at the end of a 2-day reaction time at 80°C ($4 \times 10^{-2}\,M$ catalyst, 1 atm pressure); solvent fractions collected also gave no trace of product. The remaining sticky orange residue showed an ir peak at 1950–55 cm^{-1}, which is thought to be due to a carbonyl formed by decarbonylation of the DMA. Infrared bands at 2960, 2925, 2865, 1460, and 1380 cm^{-1} were attributed to an aliphatic hydrocarbon. By heating the residue to 200°C *in vacuo*, small amounts of a clear condensible liquid were obtained; the ir identified it as the aliphatic hydrocarbon, and the strength of the methyl peaks (1380 cm^{-1}) indicated considerable chain branching. Detection of any olefinic structure in the ir was hampered by the presence of sublimed triphenylphosphine in the condensed oil.

We have been unable to isolate any characterizable complexes from the final, inactive yellow solutions, although, after removing the ethylene atmosphere, addition of hydrogen at room temperature rapidly regenerates the violet color of the starting catalyst. However, an inactive solution containing $3 \times 10^{-3}\,M$ catalyst was reactivated by the hydrogen treatment to only about 40% of its maximum activity.

On exposure to air, both the amber solutions present during the active linear uptake region, and the inactive yellow solutions, rapidly turned green.

Solutions of $RuCl_2(PPh_3)_3$ were completely inactive for the ethylene polymerization. $HRuCl(PPh_3)_3$ formed *in situ* in dilute solutions according to reaction 1 was also inactive.

Butadiene Polymerization

The initial part of a butadiene uptake plot at 80°C using the hydride catalyst is shown in Fig. 5. The violet solution immediately turned yellow on addition of the diene, and no autocatalytic region was observed. The rate decreased with time, but the initial rate was some 200 times greater than the linear region of the ethylene uptakes for corresponding conditions. Some initial rate data for the butadiene system are given in Table 1. After 1 hr, when some 400 moles of diene per Ru had been consumed (for the conditions of Fig. 5), the reaction rate had decreased from the initial value of $36.1 \times 10^{-5}\,M\mathrm{s}^{-1}$ to a value of $2.20 \times 10^{-5}\,M\mathrm{s}^{-1}$ which then remained constant for several hours before slowly decreasing. Initial rate data indicated a first-order dependence on ruthenium but, in contrast to the ethylene system, the rate was now independent of the substrate concentration. The unimolecular rate constants (k_2) estimated for the butadiene system are given in Table 2. A good Arrhenius plot yielded the activation parameters, $\Delta H\ddagger = 27.8 \pm 1.9$ kcal mol^{-1} and $\Delta S\ddagger = 21.0 \pm 6.0$ e.u.

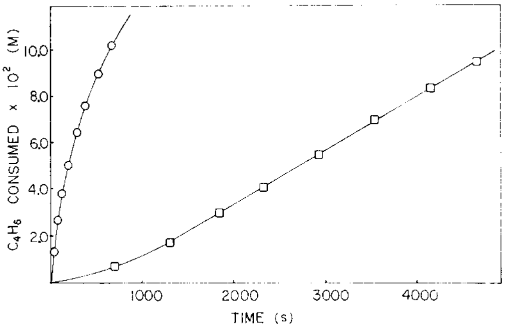


FIG. 5. Butadiene uptake plots at 80°C; 725 mm C_4H_6, $5.0 \times 10^{-4}\,M$ Ru. Catalyst: ○ $HRuCl(PPh_3)_3DMA$; □ $RuCl_2(PPh_3)_3$.

During the rapid butadiene uptake, the DMA solutions quickly became cloudy, and the oil droplets which were formed coalesced to a gel on cooling. The gel, while soft, was partially soluble in dichloromethane or carbon disulfide; the gel became semisolid on standing in air for several days. Infrared analysis of the polymer (in carbon disulphide) indicated approximately equal percentages of vinyl, *cis*-vinylene, and *trans*-vinylene linkages.

Addition of triphenylphosphine (phosphine:Ru = 5) decreased the initial polymerization rate by a factor of ~5, but no change in the microstructure of the isolated product was observed.

Following a polymerization reaction, if the butadiene was pumped off and replaced by 1 atm hydrogen, rapid gas uptake was observed at 80°C. At the stage when this rate had slowed to ca. 20% of its initial value, an ir of the gel product indicated that ca. 50% of all three types of olefinic linkages had been hydrogenated.

The dichloro complex $RuCl_2(PPh_3)_3$ was also found to catalyze the formation of polybutadiene (Fig. 5). Addition of butadiene to the brown solution of the dichloro complex resulted in immediate production of a yellow coloration. The uptake rate increased for 1200 sec, and then remained linear for some hours; this linear rate ($2.32 \times 10^{-5}\,M s^{-1}$ for the conditions of Fig. 5) corresponded closely to that of the linear region observed with the hydride-catalyzed reaction at the same conditions and concentrations (see above). Infrared analysis of the gel product obtained from the reaction catalyzed by $RuCl_2(PPh_3)_3$ indicated the same relative percentages of the three types of polybutadiene linkages as found in the product of the hydride-catalyzed reaction.

Reaction of HRuCl(PPh₃)₃ with Ethylene, and Butadiene, at 25°

Color changes were observed on subjecting DMA solutions of the hydride to the olefinic substrates at the polymerization temperatures. Some quantitative measurements were made at 25°C by following changes in optical density at 520 nm, the absorption maximum of the hydride. The observed rapid loss of the hydride color was analyzed in terms of reaction 3 (*6, 7*), the resulting ethyl or butenyl complex having no significant absorption at this wavelength:

$$HRuCl(PPh_3)_2 + C_2H_4(\text{or } C_4H_6) \overset{K}{\rightleftharpoons} C_2H_5(\text{or } C_4H_7)RuCl(PPh_3)_2. \quad (3)$$

Using $7.4 \times 10^{-4}\,M$ hydride solutions and ethylene pressures up to 1 atm ($[C_2H_4] = 7.3 \times 10^{-2}\,M$ atm^{-1}), K for ethylene was estimated to be $11.6\,M^{-1}$; the ethyl complex is thus approximately half formed at 1 atm C_2H_4 and 25°C. Butadiene complexes much more strongly and, even at 30 mm pressure ($[C_4H_6] = 1.6\,M$ atm^{-1}), the hydride color is completely removed; this puts K for butadiene $> 200\,M^{-1}$. We have no evidence for the existence of the probable hydride–olefin intermediate in reaction 3.

During the spectrophotometric investigation of reaction 3 for ethylene, a very much slower fading of the hydride color occurred following the rapid decrease due to the K equilibrium. This slow fading gave strictly linear log(optical density) vs time plots, showing a first-order dependence on the hydride concentration remaining after reaction 3 has taken place; the pseudo-first-order rate constant was determined as 2.8×10^{-5} s^{-1}.

Spectrophotometric measurements at 25°C showed that $RuCl_2(PPh_3)_3$ also complexes with ethylene and butadiene. The equilibrium constants appear to be of the same order of magnitude as those determined for reaction 3, but the systems are more complicated because of partial loss of chloride ligand, as well as loss of triphenylphosphine, from the $RuCl_2(PPh_3)_3$ complex (*14*). Other workers have reported on the interaction of olefins with this complex [see ref. (*11*)].

DISCUSSION

The maximum polymerization rates are first-order in the ruthenium hydride catalyst; the ethylene system is first-order in ethylene, while the butadiene system is independent of the diene concentration. These dependences can be explained in terms of a common mechanism for both systems, if the stronger complexing of the diene (possibly as a chelate) is taken into account.

Ethylene is seen to initially complex weakly with the hydride to give an alkyl [Eq. (3)]. The rate-determining step in the subsequent polymerization then involves interaction of the ethyl complex with further ethylene. The initial curved reaction region (Fig. 1) is attributed to a build up of alkyl concentration as the reaction proceeds, for example:

$$\mathrm{HRu} + \mathrm{C_2H_4} \overset{K}{\rightleftharpoons} \mathrm{Ru{-}C_2H_5} \xrightarrow[k_1]{C_2H_4} \text{products.} \quad (4)$$

The slow fading of the hydride color after the initial K equilibrium at 25°C must give a measure of the subsequent polymerization rate at this temperature. Assuming a first-order dependence on ethylene, which, at $7.3 \times 10^{-2}\,M$, is present in large excess in the spectrophotometric study, gives a second-order rate constant of $3.8 \times 10^{-4}\,M^{-1}\mathrm{s}^{-1}$; extrapolation of the Arrhenius plot for the k_1 data in Table 2 yields a k_1 value of $2.8 \times 10^{-4}\,M^{-1}\mathrm{s}^{-1}$ at 25°C. Considering the lengthy extrapolation, the agreement between these values is good.

Evidence for the existence of the ethyl complex in solution is seen by the fact that in the presence of acid (HCl), ethane is produced in a stoichiometric reaction (*14*) and no polymerization is observed:

$$(\mathrm{C_2H_5})\mathrm{RuCl(PPh_3)}_n + \mathrm{HCl} \rightarrow \mathrm{C_2H_6} + \mathrm{RuCl_2(PPh_3)}_n;\ n = 2 \text{ or } 3. \quad (5)$$

Following the reaction schemes of Cramer (*5*), the slow reaction in the polymerization may be written as follows:

$$\mathrm{Ru{-}C_2H_5} + \mathrm{C_2H_4} \overset{K'}{\rightleftharpoons} (\mathrm{C_2H_4})\mathrm{Ru(C_2H_5)} \xrightarrow{k'} \mathrm{Ru{-}CH_2CH_2C_2H_5}. \quad (6)$$

Coordination of a second ethylene, like the first addition to the hydride complex, is likely to be fast, and the subsequent insertion reaction is likely to be slow (k'). Continuation of the processes outlined in Eq. (6) gives rise to a growing alkyl chain. The extended linear uptake region observed indicates that the reactivities of the various intermediate alkyls are very similar; this linear rate can thus be written as $k'K'[\mathrm{C_2H_4}][\mathrm{Ru(alkyl)}]$ and the estimated second-order rate constants are, in fact, $k'K'$ values (see below).

The rate-law arising from the mechanism outlined in Eq. (6) is given in the general case by:

$$d[\mathrm{C_2H_4}]/dt = k'K'[\mathrm{C_2H_4}][\mathrm{Ru}]_{\mathrm{Total}}/(1 + K'[\mathrm{C_2H_4}]). \quad (7)$$

The very slight curvature in the ethylene dependence (Fig. 3) could be real and be in accord with Eq. (7). However, to a good approximation, the rate-law takes the limiting from $k'K'[\mathrm{C_2H_4}][\mathrm{Ru}]$; the K' equilibrium must lie well to the left at the reaction conditions, that is, $K'[\mathrm{C_2H_4}] \ll 1$, and thus K' has to be $\ll 25\,M^{-1}$ since $[\mathrm{C_2H_4}] \approx 4 \times 10^{-2}\,M$. This seems reasonable considering the equilibrium constant for reaction of ethylene with the hydride [Eq. (3)] is $11.6\,M^{-1}$ at 25°C, and that such equilibrium constants usually decrease with increasing temperature (see below). Analysis of the ethylene dependence of Fig. 3 according to Eq. (7), by plotting $(\text{rate})^{-1}$ vs $[\mathrm{C_2H_4}]^{-1}$, does in fact give an excellent straight line, and yields values of $k' = 1.1 \times 10^{-2}\ \mathrm{s}^{-1}$ and $K' = 6.9\,M^{-1}$. Similarly, the data for the ethylene dependence at 70°C (Table 1) can be analyzed to give $k' = 0.6 \times 10^{-2}\ \mathrm{s}^{-1}$ and $K' = 5.6\,M^{-1}$ at this temperature. However, the breakdown of the k_1 value into k' and K' for the ethylene system is not justified considering the very slight curvature in Fig. 3, which more likely results from increasing loss of the catalyst by oxygen impurity with increasing ethylene pressure.

Butadiene completely removes the hydride color at the start of the reaction, i.e., equilibrium 3 lies well to the right, and presumably a butenyl complex exists in solution—no initial curved region is seen in the uptake plot (Fig. 5). The kinetic data can again be interpreted in terms of the mechanism outlined in Eq. (6), and the rate-law shown in Eq. (7). The essential independence of the rate on $[\mathrm{C_4H_6}]$ implies however that $K'[\mathrm{C_4H_6}] \gg 1$. One factor affecting the predominance of this term in the denominator of Eq. (7) is the butadiene solubility ($\sim 1.0\,M\ \mathrm{atm}^{-1}$) which is about 25 times that of ethylene. Since the butadiene polymerization rate is still independent of the butadiene concentration at 166 mm, this requires that $K' \gg 5\,M^{-1}$ for this system. Considering the measured equilibrium constant ($>200\,M^{-1}$ at 25°C) for reaction with the hydride, this seems reasonable. Thus, compared with the ethylene system, both factors in the $K'[\text{olefin}]$ term are very much larger, and the rate-law takes the limiting form, $k'[\mathrm{Ru}]$, for the butadiene system. The k_2 values listed in Table 2 for the diene system are thus

k' values, and are a direct measure of the insertion rate [Eq. (6)].

It should be noted that the above analysis leads to the conclusion that reaction of the hydride with butadiene (investigated spectrophotometrically) leads to the production of a butenyl–butadiene species, $(C_4H_6)Ru(C_4H_7)$, and that the measured equilibrium constant, in fact, refers to a KK' value for a reaction with two butadiene molecules [Eqs. (3) and (6)]. The data imply more correctly that $KK' > 3000\,M^{-2}$.

Comparison of the data in Table 2 shows that, at about 65°C and 1 atm of substrate, the polymerization rate for butadiene (k') is some 15 times greater than that for ethylene ($k'K'$). The rate of the actual insertion step (k') is thus probably at least 50 times higher for the butadiene system.

The activation parameters determined for the ethylene system ($\Delta H\ddagger = 20.0$ kcal mol^{-1}, $\Delta S\ddagger = -7.7$ e.u.) must apply to the composite constant $k'K'$, although the rate constant is expected to be much more temperature-dependent than K'. The parameters may be compared to those reported (*5*) for ethylene dimerization catalyzed by rhodium chlorides in HCl–ethanol media (16.6 kcal mol^{-1}, -20.1 e.u.), which were said to refer to the following insertion reaction:

$$C_2H_5Rh(C_2H_4)Cl_3^- \xrightarrow{k} C_2H_5CH_2CH_2RhCl_3^-. \quad (8)$$

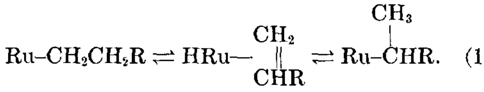
The activation parameters for the rhodium system appear, in fact, to apply to a composite constant kK_e, where K_e refers to the pre-equilibrium

$$C_2H_5RhCl_3^- + C_2H_4 \overset{K_e}{\rightleftharpoons} C_2H_5Rh(C_2H_4)Cl_3^-. \quad (9)$$

K_e was measured and decreased with increasing temperature; from the data presented, the thermodynamic parameters $\Delta H \approx -4$ kcal, $\Delta S \approx -6.0$ e.u. may be estimated (K_e was $10\,M^{-1}$ at -10°C). Allowing for the pre-equilibrium, the activation parameters for k would be closer to 21 kcal mol^{-1} and -14 e.u. Presumably corrections of a similar magnitude could be made to our measured activation parameters. Activation parameters of 12.2 kcal mol^{-1} and -14.9 e.u. have been reported for the propagation step in an ethylene polymerization catalyzed by a soluble titanium Ziegler catalyst in toluene (*15*).

The parameters obtained for the butadiene system ($\Delta H\ddagger = 27.8$ kcal mol^{-1}, $\Delta S\ddagger = 21$ e.u.) refer directly to the insertion reaction [cf. Eq. (6)]. Comparison of the data shows that the activation energy for the butadiene system is likely greater than that for the ethylene system, and this is feasible considering the butadiene coordinates (possibly as a chelate) more strongly than the ethylene. The factor responsible for the greater rate of the insertion reaction with the butadiene system is the much more favorable entropy of activation. Such an effect could be related to the breaking of a butadiene chelate ring in the transition state required for the overall insertion, or perhaps a reduction in the degree of solvation of the transition state complex in this polar medium.

The high degree of chain branching in the ethylene polymer could arise through isomerization via an alkyl complex [cf. Eq. (4)]:



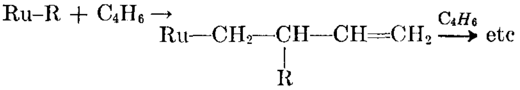
$$Ru\text{-}CH_2CH_2R \rightleftharpoons HRu\text{—}\begin{matrix}CH_2\\ \| \\ CHR\end{matrix} \rightleftharpoons Ru\text{-}\overset{CH_3}{\overset{|}{C}}HR. \quad (10)$$

A butene-1 ⇌ butene-2 isomerization process has been shown to be very fast under the conditions of ethylene dimerization at a rhodium center; that is, isomerization is much faster than insertion (*5*).

Product release could occur from a hydrido–olefin intermediate formed as in Eq. (10); or via an intramolecular hydrogen transfer in an alkyl–ethylene intermediate, e.g.:

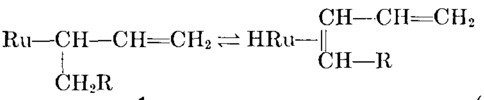
$$Ru\text{-}CH_2CH_2R \xrightarrow{C_2H_4} (C_2H_4)Ru\text{-}CH_2CH_2R \rightarrow (C_2H_5)Ru + CH_2{=}CH\text{—}R. \quad (11)$$

Similar reaction schemes can be written for the butadiene system. A reaction such as Eq. (4) can now give two possible butenyl intermediates depending on whether the hydrometalation is Markownikoff or anti-Markownikoff, i.e., $Ru\text{-}CH(CH_3)CH{=}CH_2$ or $Ru\text{-}CH_2CH_2CH{=}CH_2$, respectively. Subsequent propagation reactions corresponding to Eq. (6) with overall addition of the Ru–R moiety (R = butenyl, etc.) across the butadiene unsaturated bonds in either direction, and product release via a reaction such as Eq. (10), can give produce, containing vinyl and vinylene linkages, for example:



$$\mathrm{Ru{-}R + C_4H_6 \rightarrow Ru{-}CH_2{-}\underset{\displaystyle R}{\underset{|}{CH}}{-}CH{=}CH_2 \xrightarrow{C_4H_6} etc}$$

and/or

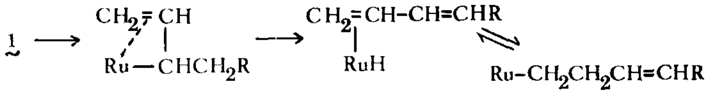


$$\mathrm{Ru{-}\underset{\displaystyle CH_2R}{\underset{|}{CH}}{-}CH{=}CH_2 \rightleftharpoons HRu{-}\Big\Vert\begin{matrix}CH{-}CH{=}CH_2\\ CH{-}R\end{matrix}} \qquad (12)$$

1

(where R is *initially* $-CH_2CH_2CH{=}CH_2$ or $-CH(CH_3)CH{=}CH_2$).

An intramolecular hydrogen transfer according to Eq. (11), and involving intermediate **1** with further coordinated butadiene, can also give rise to vinylene products. Further, the possibility of σ–π intermediates, which have sometimes been postulated for catalytic reactions involving conjugated dienes (*16*), cannot be ruled out. For example,

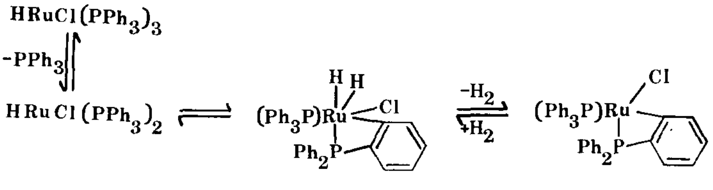


(13)

The inhibition of polymerization by added chloride or triphenylphosphine shows the importance of available coordination sites on the metal complex. The phosphine inhibition likely results from decreased dissociation according to Eq. (2); similar inhibition is observed in catalytic hydrogenations using this ruthenium complex (*6, 7*).

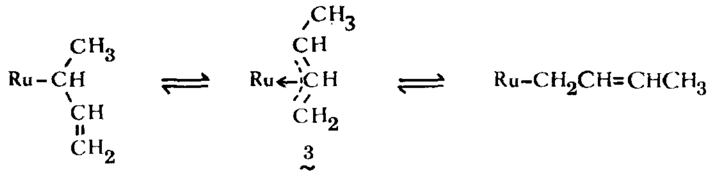
It is significant that polybutadiene with the same microstructure is obtained from reactions catalyzed by both the hydride complex $HRuCl(PPh_3)_3$ and the dichloro complex $RuCl_2(PPh_3)_3$. The initiation period required for the dichloro complex is almost certainly due to formation of the hydride by a reaction with butadiene; that the two systems eventually give extended linear regions of essentially equal rates ($2.20 \times 10^{-5}\,Ms^{-1}$ for $HRuCl(PPh_3)_3$, and $2.32 \times 10^{-5}\,Ms^{-1}$ for $RuCl_2(PPh_3)_3$) indicates the same catalytic species are present. The dichloride is inactive for ethylene polymerization, presumably because the hydride is not formed. Canale and coworkers (*17*) have used 6:1 PPh_3-$RuCl_3$ systems at 25°C in aqueous emulsion to polymerize butadiene; these workers suggested possible initiation through a metal–hydride complex, and steric control effected through a metal–diene complex. The microstructure of the polymer we obtained is somewhat similar to their product.

Some deactivation of the catalytic system undoubtedly arises from decarbonylation of the solvent which gives less active ruthenium carbonyl species. However, the observations that (a) deactivation occurs much more readily in the butadiene reaction than in the ethylene reaction under the same conditions; and (b) the activity can be regenerated to ca. 40% of its initial value by treatment of the inactive solution with hydrogen, rules out decarbonylation as the major cause of deactivation. The $HRuCl(PPh_3)_3$ complex in solution is known to undergo a reversible intramolecular H_2 elimination, via a process involving the ortho hydrogen of a phenyl ring of the coordinated phosphine [e.g., ref. (*18*)]:



(14)

A similar reaction has been postulated for the $(C_2H_5)RuCl(PPh_3)_2$ complex, with the final irreversible elimination of ethane, to account for a stoichiometric hydrogenation of ethylene in the absence of molecular hydrogen (*19*). Deactivation for polymerization (and the regeneration by H_2) could result from formation of a complex such as 2. Further, the butadiene system could give rise to inactive π-allyl intermediates, for example:



(15)

Again, the hydride catalyst could be regenerated along with butenes by hydrogen treatment of 3. Since we have been unable to characterize the final inactive ruthenium complex, definite conclusions regarding the deactivation cannot be made. Further, the possibility that the butadiene polymerization initially involves reaction of 3 with the diene, a reaction which is well-known in palladium chemistry (*20*), cannot be excluded.

Although vinyl fluoride was not polymerized by the violet $HRuCl(PPh_3)_3$ solutions at 80°C, a yellow coloration was produced rapidly, and this suggests that the fluoroalkyl complex is thermodynamically too stable to react with further substrate.

Further kinetic studies on related systems investigating ligand, substrate, and solvent effects, and molecular weight distribution measurements on the polymers, are in progress, and should help elucidate further the factors controlling the rate-determining step(s).

The partial hydrogenation of the butadiene polymer on subjecting the system to a hydrogen atmosphere is of interest. The hydrogenation is presumably catalyzed by the $HRuCl(PPh_3)_3$ complex (*6*, *7*). Such reductions catalyzed by homogeneous Ziegler catalysts are well known (*21*).

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