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A Catalytic Codimerization of Ethylene and *n*-Butenes by a Nickel Complex in Solution

G. G. EBERHARDT AND H. K. MYERS

Sun Oil Company, Marcus Hook, Pennsylvania 19061

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A catalytic codimerization reaction of ethylene and *n*-butenes was investigated. The soluble catalyst is prepared *in situ* by the reaction of a nickel coordination complex with an excess of ethylaluminum sesquichloride in chlorobenzene or toluene solution. A C_6 codimer is formed with a selectivity of more than 85%. The codimers are almost exclusively olefinic derivatives of 3-methylpentane.

INTRODUCTION

Numerous transition metal coordination complexes, particularly of Group VIII metals, have been found to catalyze dimerization reactions of monoolefins, involving various degrees of catalytic activity and selectivity. Generally transition metal hydride derivatives have been shown or postulated as key catalytic intermediates. In recent years, several systems involving soluble nickel complex catalysts have been reported (*1*) and extraordinary high rates of reaction and varying product selectivities, depending on the nickel complex compounds used, have been noted. Although many different monoolefins dimerize in these systems, their individual reactivities are quite different; ethylene and propylene are generally most reactive. The higher olefins react much slower and double-bond shifts occur simultaneously with the dimerization. The codimerization of olefins has been carried out successfully in these systems and the product distribution is determined by statistical factors. Ethylene and propylene, olefins of nearly equal reactivities, yield a maximum C_5 codimer fraction of only 55% under certain conditions (*1*b,d). However, olefins whose individual reactivities differ by an order of magnitude can be codimerized in high yields under conditions which depend mainly on the relative concentration of the two monomers in solution. Here, results obtained from the codimerization of *n*-butene (thermodynamic equilibrium mixture) with ethylene using a soluble nickel coordination catalyst are discussed. This catalyst system was previously described (*1*e) for the selective dimerization of propene. It consists of a nickel coordination complex:

$$(R)_3R'P\,[(R_3P)NiCl_3], \qquad (1)$$
$$R = \text{isopropyl}; \qquad R' = \text{benzyl}$$

which, in conjunction with excess ethylaluminum sesquichloride in the proper solvent (chlorobenzene, toluene), leads to an active catalytic species of undetermined composition.

EXPERIMENTAL METHODS

A. Materials

Fischer, certified grade, chlorobenzene or toluene, stored over molecular sieves, was used as a solvent. The *n*-butene (8% 1-butene, 44% *cis*-2-butene, 48% *trans*-2-butene) was obtained from Matheson and distilled from small amounts of triethylaluminum for purification. The ethylene (Matheson, c.p. grade) was passed through a molecular sieve drying tower before use. Ethylaluminum sesquichloride (Ethyl Corp.) was handled via syringe technique from a 1 *M* solution in toluene.

B. Reaction Procedure

The general apparatus and procedure has been described before (*1*e). The different temperature levels necessary for the formation of the "active species" (25–35°C) and for the codimerization reaction (−10°C) are of importance to obtain reproducible results. The reaction temperature of −10°C was chosen primarily as a matter of convenience to handle liquefied C_4 olefins in a glass apparatus. The following experimental modifications were made to carry out the codimerization reaction. 0.05 mmole (28.5 mg) of the nickel catalyst complex (*1*) was dissolved in 50 ml of degassed chlorobenzene under N_2 protection in the reaction flask. 1.25 mmole of $(C_2H_6)_3Al_2Cl_3$ (1 *m* in toluene), Al:Ni ratio: 50:1, were added via syringe to the rapidly stirred catalyst solution at room temperature (25°C). A color change from blue to clear yellow was noted instantly. After 60 sec *n*-butene gas was introduced rapidly through a syringe needle into the stirred solution and a slight exotherm was noted. The temperature read 30°C within 10–20 sec at which point external dry ice/acetone cooling was applied to lower the inside temperature to ca. −20°C. The rapid addition of *n*-butene was continued until 1 *M* was condensed into the reaction mixture (ca. 10 min). The reaction temperature now was adjusted to −10°C and kept at this level. The system was allowed to equilibrize for 45 min to obtain the thermodynamic double-bond equilibrium for this temperature. At this point, a sample was taken for VPC analysis. A small amount of C_8 butene dimer (ca. 10%) had formed and is accounted for in the successive codimer analysis. Immediately following the sample removal, ethylene gas was introduced via a syringe needle at a desired feed rate into the liquid phase under rapid agitation. At favorable codimerization rates, the total partial pressure was less than atmospheric and a N_2 gas line was connected to the system and set at a 860 mm Hg relief valve. The reaction was terminated (addition of 1 ml isopropanol) without prior interruption of the ethylene feed after the introduction of 0.33 *M* ethylene and the product mixture was analyzed by VPC technique. The individual experiments were fairly well reproducible; however, the data points were usually average values obtained from several repeat experiments.

C. The Nickel Complex Catalyst

Its preparation and properties have been described before (*1*e).

RESULTS

In the context of a codimerization of ethylene and *n*-butene, the dimerization reactivity of the individual olefins is of interest. The dimerization of butene-1 with the above catalyst system was, therefore, studied and the results obtained are shown in Fig. 1. The butene-1 (1 *M*) was rapidly condensed in the activated catalyst solution as described in the Experimental Methods. A very fast concurrent dimerization reaction was noted and efficient cooling is necessary to maintain the reaction temperature of −10°C. A 20% conversion was already reached at the end of the butene-1 addition (10 min). Thereafter samples were taken for analysis and a rapid decline in the rate of dimerization was noted. A constant equilibrium rate was reached after ca.

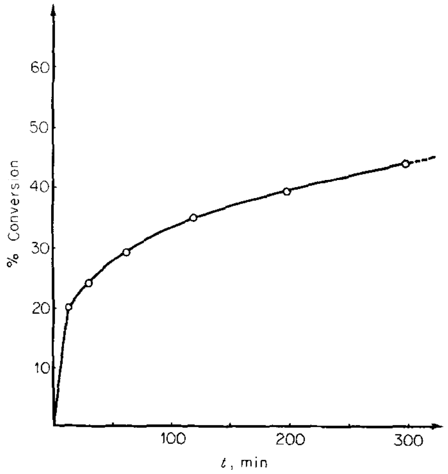


FIG. 1. Butene-1 (1 *M*) dimerization with the $PR_4[PR_3NiCl_3]/Et_3Al_2Cl_3$ catalyst system: 0.05 m*M* Ni complex in 50 ml chlorobenzene and an Al/Ni ratio of 50. Activation temperature 25–30°C for 2 min. Reaction temperature −10°C.

60 min. The composition of the C_4 olefin reactant is as follows:

Time (min)	Butene-1	*cis*-Butene-2	*trans*-Butene-2
10	4.6	55.4	40.0
22	3.6	43.0	53.4
45	2.7	33.3	64.0

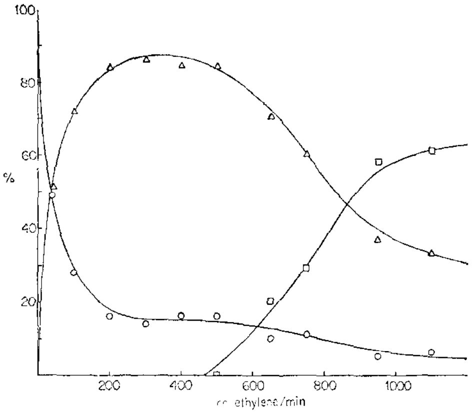


Fig. 2. The product distribution of a *n*-butene–ethylene codimerization as a function of various ethylene feed rates: (△) C_6; (○) C_8; (□) C_4 olefin. Reactants: 1 mole of *n*-butene and up to 0.33 mole ethylene. Catalyst: 0.05 m*M* $R_4P[(R_3P)NiCl_3]$ 0.25 m*M* $Et_3Al_2Cl_3$ in 50 ml chlorobenzene activated at +25 to +30°C and reacted at −10°C.

The dimerization products are C_8 olefins of undetermined structural composition. As can be seen, the very fast initial dimerization of butene-1 is accompanied by a rapid double bond isomerization. At the end of the butene-1 addition, isomerization has proceeded far with a preferential formation of *cis*-butene-2. Subsequently, a complete thermodynamic double-bond equilibration is reached in less than 1 hr. The high initial rate of dimerization is apparently linked to a high concentration of butene-1. The constant and much slower equilibrium rate obtained after 1 hr involves a reactant composed of the *n*-butene thermodynamic equilibrium mixture at this temperature. This equilibrium rate calculates to ca. 0.7 kg dimer/g Ni/hr. This number is based on the weight amount of Ni introduced as the catalyst precursor, since the concentration of the active species in solution is not known. The rate is more than 2 orders of magnitude lower than that of propylene under comparable conditions in this system. The rates of ethylene dimerization were shown to be still higher in similar catalyst systems (*1*b,d). This large reactivity difference of ethylene versus the *n*-butene equilibrium mixture is a favorable precondition for their selective codimerization. A large excess of *n*-butenes is required in conjunction with a very low ethylene concentration as determined by its controlled feed rate. The *n*-butene mixture (1 *M*) was condensed in the activated catalyst solution as described in Experimental Methods and after a 45 min equilibration period ethylene gas was introduced into the liquid phase with efficient agitation at various constant feed rates up to a consumption of 0.33 *M* of ethylene. The product composition was then determined by VPC analysis. As shown, even at very low ethylene feed rates and a correspondingly low equilibrium concentration, the formation of C_8 dimers diminishes rapidly and increasing amounts of a C_6 olefinic codimerizate are produced. An optimal value of more than 85% codimer is reached at ethylene feed rates of 300–400 ml/min under these conditions involving a net consumption of *n*-butenes. At ethylene feed rates of 500 ml/min and more the relative amount of codimer decreases and the formation of *n*-butenes derived from the dimerization of ethylene gradually predominates. This *in situ* ethylene dimerization, which occurs for statistical reasons gradually at all feed rates, gives primarily butene-1 which then can be subjected to double-bond isomerization concurrently. Thus, the *n*-butene composition in the reaction will be somewhat different from the thermodynamic equilibrium value, particularly at higher ethylene feed rates. Trace amounts (3% or less) of undetermined C_{10} olefins are also formed but not indicated on the graph. The C_6 codimer product composition is shown in Table 1. As shown, more than 95% of the codimer fraction is olefinic derivatives of the 3-methylpentane parent hydrocarbon structure. The thermodynamic double-bond equilibrium of this group of olefins

TABLE 1
COMPOSITION OF C, CODIMER FRACTION A VARIOUS ETHYLENE FEED RATES AS SHOWN IN FIG. 2

Ethylene feed rate (ml/min)	260	530	660	620[a]
% *trans*-3-Methylpentene-2	52.0	48.4	41.0	39.5
% *cis*-3-Methylpentene-2	14.3	12.2	9.7	9.5
% 2-Ethyl-butene-1	20.4	24.0	29.8	29.7
% 3-Methyl-pentene-1	10.7	12.0	14.2	17.1
% *trans*-Hexene-2	1.4	1.8	2.8	2.2
% *cis*-Hexene-2	1.2	1.6	2.5	2.0
Rate: kg C_6 + C_8/g Ni/hr	13	20	21	16

[a] Toluene solvent.

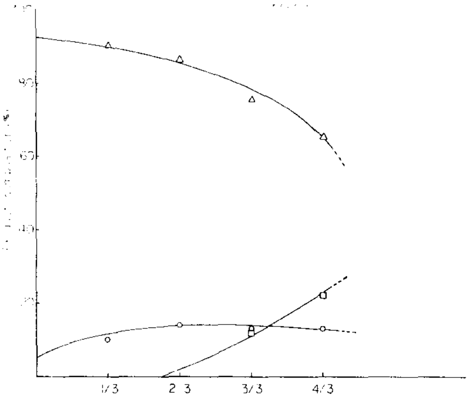
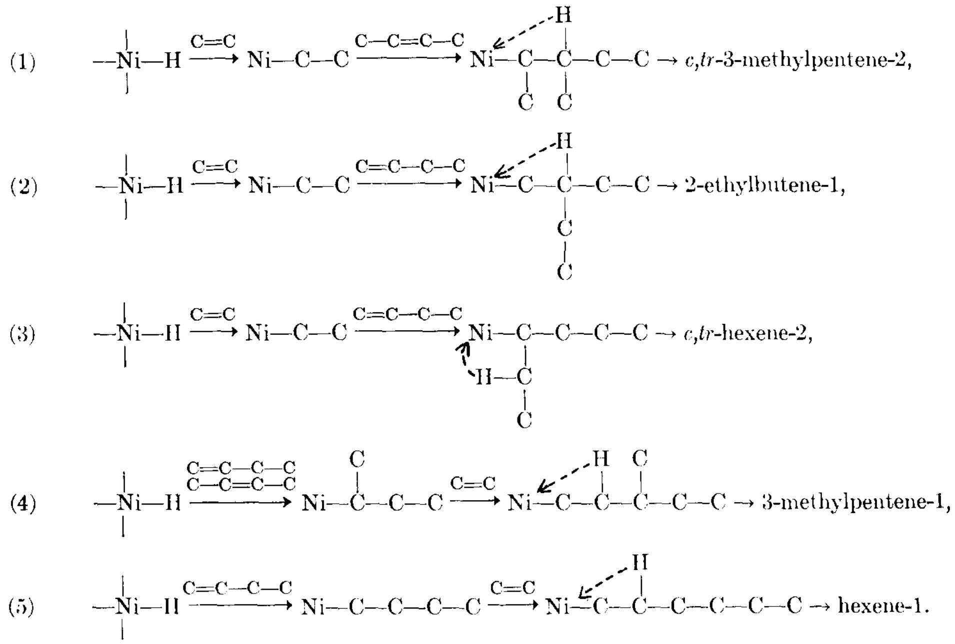


FIG. 3. Product composition as a function of conversion at const. ethylene feed rate of 300 ml/min. Conditions and explanation as in Fig. 2.

(3-methylpentene-2,3-methylpentene-1,2-ethylbutene-1) is by far (*2*) favoring 3-methylpentene-2 (>95%) at this temperature. Thus, the codimer olefins have not reached the thermodynamic double-bond equilibrium and are at least partially primary products. The rates of reaction are, of course, linked to the ethylene feed rates and the use of toluene solvent leads to a slight decrease in the codimerization rate. The continued addition of ethylene to the system leads to a deactivation of the highly sensitive catalyst via the introduction of trace impurities as was shown before in the dimerization of propylene. This decrease in the active catalyst concentration by deactivation as well as dilution by product formation leads to a change of the codimer selectivity as a function of conversion as illustrated in Fig. 3. A considerable change in the product composition is noted at high conversion levels and decreased catalyst activity, which effects the relative C_4/C_2 concentration.

DISCUSSION

The dimerization of butene-1 was shown to occur rapidly; however, the reactant olefin is also subjected to a fast double-bond equilibration concurrently. The formation of the thermodynamic *n*-butene equilibrium mixture eventually leads to a much lower rate of dimerization typical for this composition. It cannot be said at this point whether this dimerization involves the butene-1 only, which could be refurnished continuously from the equilibrium pool or whether *cis* and *trans* butene-2 can participate directly in the dimerization reaction. As discussed below, it is likely that both reactions may occur simultaneously. In any case, the low reactivity of the *n*-butene mixture and the very high reactivity of ethylene in this system is desirable for a selective codimerization of these monomers. An optimal codimerization requires a very high *n*-butene to ethylene ratio, which, at a given temperature and catalyst concentration, can be conveniently obtained by a controlled feed of ethylene to the liquid reaction mixture, containing a large excess of *n*-butene. A C_6 codimer selectivity of better than 85% can readily be achieved (Fig. 2). The C_6 olefins are mainly (>95%) derived from the 3-methylpentane parent hydrocarbon; however, the individual double-bond isomers are far different from the thermodynamic equilibrium value (Table 1). This fact indicates that the codimer olefins are not readily subject to double-bond equilibration in the presence of large concentrations of the monomer olefins. A similar situation was noted in the propylene dimerization system where the dimers obtained in the presence of the reacting propene monomer are to more than 95% the thermodynamically less favored 1-olefins. Apparently the higher terminal olefins cannot readily reenter the coordination sphere of the nickel catalyst complex in the presence of the more strongly coordinating olefins: ethylene, propylene, *n*-butene. Thus, no fast catalyst/product olefin interaction occurs which would be a precondition for a double-bond shift. The *in situ* formation of a highly labile and reactive nickel hydride complex as key catalyst intermediates has been suggested before by us and other authors (*1*). Based on this assumption, the following simplified mechanistic scheme can be visualized:



This scheme involves three well-known organometallic reactions: metal hydride olefin addition, metal–carbon olefin insertion and β-hydrogen elimination. All the possible olefins derived from this scheme are formed in the actual codimer product with the exception of hexene-1. The major portion of the codimers (80–90%) is derived from the sequence 1, 2 and 3. They all involve the primary reaction of ethylene which is not inconsistent with the high reactivity and coordinating ability of this olefin. The main product component, 3-methylpentene-2, could be derived from sequence 1 which involves a direct participation of *n*-butene-2. In Table 1 a change in product composition is noted with increasing ethylene feed rates involving particularly a relative increase in the amounts of 2-ethylbutene-1 and 3-methylpentene-1. It was mentioned above that, with increasing ethylene concentrations (i.e., feed rates), the formation of butene-1 from ethylene is statistically more and more favored. In spite of the concurrent double-bond equilibration, the butene-1 concentration in the system, therefore, will be increasingly above the thermodynamic value. Thus, butene-1 is more readily available to enter sequence 2, 3 and 4. In agreement with this interpretation, the products derived from these sequences are indeed more predominant at higher ethylene feed rates (Table 1). The dimerization of propene leads predominantly to a double-branched 2,3-dimethylbutene-1 with soluble nickel catalysts containing a strongly basic phosphine ligand (e.g., triisopropylphosphine) as originally discovered by G. Wilke *et al.* Accordingly, the reactant monomers here can only combine to methylpentane derivatives which are the main products of the codimerization. A hypothetical "active species" derived from the catalyst components used here has been postulated previously (*1*e). An analogous mechanistic interpretation is not inconsistent with the results observed here.

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