produce a decrease in the reaction product ratio Φ, as confirmed by the experimental data.

The hole density is initially determined by the surface reaction itself, i.e., the pickup of electrons and resulting generation of holes by sorbed iodine. Complete coverage of grain surfaces throughout the pellet is reached when the conductivity attains a steady state value in about 6 min.

The equilibration of the chemical composition (stoichiometry) throughout the individual grains of the solid catalyst occurs more slowly and accounts for the time required (30 min or more) to reach a steady state in the reaction product ratio.

The absence of an effect of hydrogen on the reaction indicates that no rate-controlling step involving dissociation of hydrogen iodide, or hydrogen ion formation in the adsorbed phase is involved.

In summary, we have shown that the selectivity of a CuI catalyst is controlled by an electronic parameter. Our proposed model mechanism suggests that the hole density determines the reaction product distribution. In turn, the hole density is determined initially by the chemical reaction occurring on the catalyst surface, and can be controlled in the steady state by an applied potential.

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Olefin Dimerization over Cobalt-Oxide-on-Carbon Catalysts

III. Oligomerization of Ethylene*

In 1932 Schuster (2) reported that a cobalt-oxide-on-carbon catalyst was able to dimerize ethylene to mixed n-butenes with a high degree of selectivity. Later studies on this dimerization (3) showed that typically the products were 77% butenes, 13.8% hexenes, 4.6% octenes, 2.3% decenes, and 2.3% higher oligomers. In this work Cheney et al. found that the butene isomer distribution in the product was dependent upon the contact time in their flow system.

*For Parts I and II see ref. (1).

At a flow rate (g/liter-hr) of 72 a 74% conversion to dimer (9% 1-butene and 91% 2-butene) was found while at a flow rate of 360 a 37% conversion to dimer (70% 1-butene and 30% 2-butene) was found. The hexene isomers consisted of 10% 1-hexene, 38% cis-2- and cis-3-hexenes, 38% trans-2- and trans-3-hexenes, and the balance (14%) mixed branched chain materials containing the 3-methylpentane skeleton. The dimerization rate of propylene was found to be one-fortieth that of ethylene and that of butene-1 correspondingly

TABLE 1
OLIGOMERIZATION OF ETHYLENE OVER COBALT OXIDE ON CARBON

Catalyst:	Untreated CoO/C		Ammoniated CoO/C	
Reaction time (hr):	24		24	
Reaction temp. (°C):	25		25	
Conversion, g. prod./g. cat.:	30.9		46.2	
% of C₂H₄ fed:	74.4		94.6	
Component	% of C₄H₈	% of total product	% of C₄H₈	% of total product
Butene-1	58.8	12.2	4.6	1.2
trans-Butene-2	19.8	4.1	57.1	15.0
cis-Butene-2	21.4	4.4	38.3	10.0
Total butenes		20.7		26.2
	% of C₆H₁₂		% of C₆H₁₂	
Hexene-1	18.4	11.3	1.0	0.5
trans-Hexene-2	11.9	7.3	27.3	14.7
cis-Hexene-2	5.7	3.5	11.9	6.4
trans-Hexene-3	26.0	16.0	33.2	17.9
cis-Hexene-3	21.0	12.9	9.8	5.3
trans-3-Methylpentene-2	2.7	1.6	4.1	2.2
cis-3-Methylpentene-2	3.4	2.1	6.4	3.5
2-Ethylbutene-1 and/or 3-Methylpentene-1	10.9	6.7	6.3	3.4
Total *n*-C₆H₁₂	83.0		83.2	
Total branched C₆H₁₂	17.0		16.8	
Total hexenes		61.4		53.9
Higher olefins		17.9		19.9

C_2H_4, C_4H_8, C_6H_{12}

lower. Cheney also reported in this work that propylene–ethylene codimerization afforded product containing 30% amylene and that butene-2–ethylene codimerization gave a 50% increase in hexylenes over that obtained from ethylene oligomerization alone.

Our recently reported studies of propylene (1a), butene (1b), and hexene (1b) dimerizations using catalysts of greatly increased activity led us to reinvestigate the ethylene dimerization reaction at the milder (25°C) reaction conditions that we had previously observed to give maximum conversions. The techniques of catalyst preparation, activation, and storage and of batch olefin dimerization used in the present work have been previously described (1a). Isomer distribution analyses were made using capillary column gas chromatography with a dimethylsulfolane liquid phase and peak identifications were made by comparison with authentic samples.

RESULTS AND DISCUSSION

The results of our studies with untreated and ammonium-hydroxide-treated cobalt-oxide-on-carbon catalysts (both activated at 275°C in nitrogen) are shown in Table 1. These more active catalysts no longer possess the high selectivity for dimerization under the reaction conditions tested, the major products in both cases being the hexenes. The distribution between dimer, trimer, and higher products and the ratio of *n*-hexene to isohexene are seen to remain essentially constant even though drastic changes in olefin isomer distribution are observed. Olefin isomerization *per se* is not a factor in the formation of these products since we have previously shown that catalysts prepared in this manner are devoid of this function (1a). Olefin isomerization also would not be expected to give such high levels of the 3-hexenes (45%) in the products. However, a type of partial iso-

$$\overset{0}{Co}-H + CH_2=CH-CH_2R \; \rightleftharpoons \; \overset{CH_2 \rightleftharpoons CH-CH_2R}{\underset{0}{Co}-H} \; \rightleftharpoons \; \overset{0}{Co}-CH_2-CH_2-CH_2R$$

$$\text{I}$$

$$\overset{0}{Co}-H + CH_3CH=CHR \; \rightleftharpoons \; \overset{CH_3CH \rightleftharpoons CHR}{\underset{0}{Co}-H} \; \leftarrow \rightleftharpoons \; \overset{CH_3}{\underset{0}{Co}-CH-CH_2R}$$

$$\text{II}$$

[1]
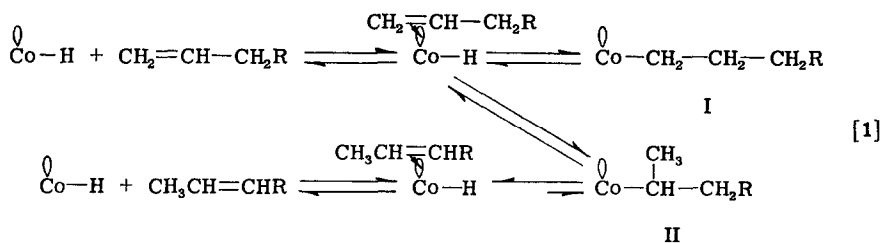
merization has been observed with 1-hexene and these catalysts (*1b*) which can be rationalized on the basis of Eq. (1). [The formalism used here has been previously described (*1a*).] Addition of any 1-olefin to an active cobalt site is possible in either of the two ways to give an *n*-alkyl cobalt (I) or a *sec*-alkyl cobalt (II) intermediate. Reversal of this addition from (I) (the favored product) can reform only 1-olefin, but 2-olefin as well as 1-olefin can be obtained in the elimination of cobalt hydride from (II). Addition of an internal olefin to this catalyst in an analogous manner is apparently very unfavorable. Partial isomerization activity has been found to be greater on the ammoniated catalysts than on the untreated catalysts and therefore the products obtained from the untreated cobalt-oxide-on-carbon catalysts are assumed to be more nearly representative of the primary products of the reaction.
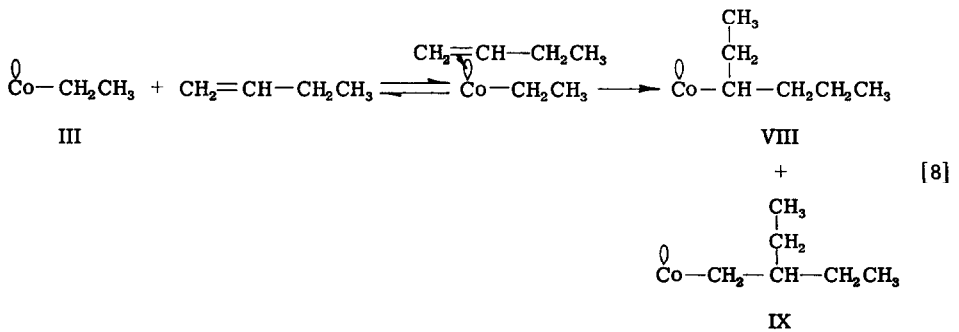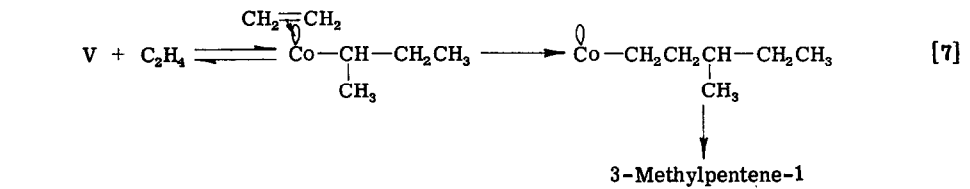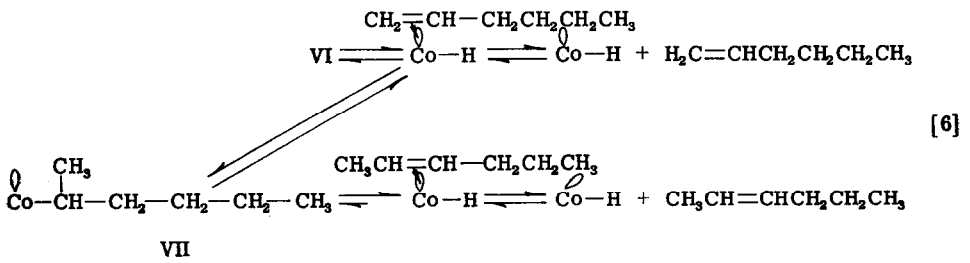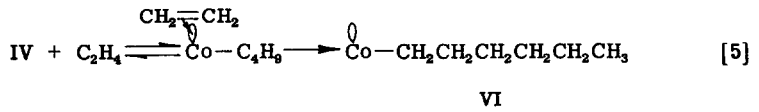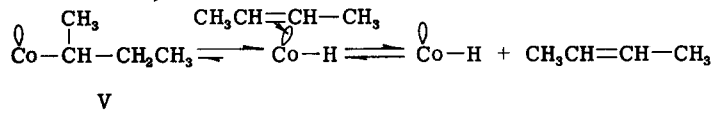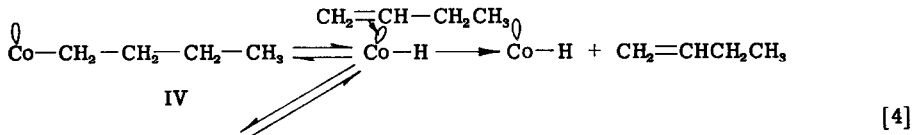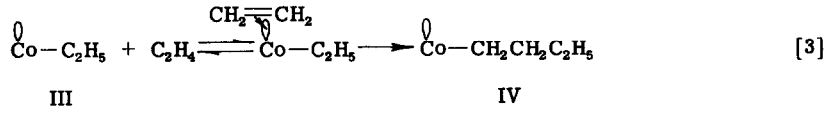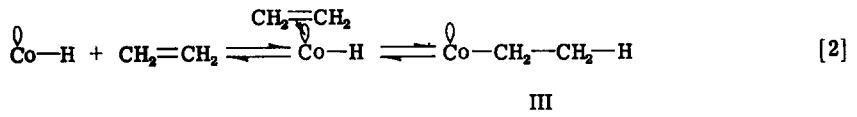
Codimerization of ethylene and propylene with the ammoniated cobalt oxide on carbon was investigated. The results are presented in Table 2. It may be seen that products from all possible combinations of olefin dimerization are found. Using the data from this table and the observation that this catalyst affords 53.6% *n*-hexenes and 46.4% isohexenes from propylene it is possible to estimate that ethylene insertion across the cobalt hydride catalytic species occurs first 76.4% of the time and propylene insertion occurs first 23.6% of the time. Correcting for differences in molar quantities present, a relative insertion preference for ethylene over propylene of only 1.7 in the first step of the reaction is indicated when catalysts of high activity are used.

A mechanism which is in agreement with these observations can be written using an insertion reaction of ethylene and butene-1

TABLE 2

CODIMERIZATION OF ETHYLENE AND PROPYLENE OVER AMMONIATED COBALT OXIDE ON CARBON[a]

Component	% of C_4H_8	% of total product
Butene-1	16.9	3.0
trans-Butene-2	46.1	8.3
cis-Butene-2	37.0	6.7
Total butenes		18.0

	% of C_5H_{10}	
3-Methylbutene-1	2.8	1.1
2-Methylbutene-1	10.0	4.0
2-Methylbutene-2	1.5	0.6
Pentene-1	5.1	2.0
trans-Pentene-2	51.0	20.4
cis-Pentene-2	29.6	11.9
Total pentenes		40.0

	% of C_6H_{12}	
4-Methylpentene-1	2.4	1.0
trans-4-Methylpentene-2	11.3	4.7
cis-4-Methylpentene-2	8.5	3.6
2-Methylpentene-1	1.0	0.4
2-Methylpentene-2	0.2	0.1
Hexene-1	1.9	0.8
trans-Hexene-2	22.6	9.5
cis-Hexene-2	13.2	5.5
trans-Hexene-3	22.4	9.4
cis-Hexene-3	7.8	3.3
trans-3-Methylpentene-2 and *cis*-3-Methylpentene-2	5.4	2.3
2-Ethylbutene-1 and/or 3-methylpentene-1	3.3	1.4
Total hexenes		42.0

[a] Ammoniated CoO on carbon activated at 275°C in nitrogen. Olefin charge: ethylene, 56% by wt (65.6 mole %); propylene, 44% by wt (34.4 mole %). Run in batch system for 24 hr at 25°C to give 41.4 g product/g catalyst (88.1% conversion of olefin feed).

$$\overset{O}{Co}-H + CH_2=CH_2 \underset{}{\overset{CH_2=CH_2}{\rightleftharpoons}} \overset{O}{Co}-H \rightleftharpoons \overset{O}{Co}-CH_2-CH_2-H \qquad [2]$$

$$III$$

$$\overset{O}{Co}-C_2H_5 + C_2H_4 \underset{}{\overset{CH_2=CH_2}{\rightleftharpoons}} \overset{O}{Co}-C_2H_5 \longrightarrow \overset{O}{Co}-CH_2CH_2C_2H_5 \qquad [3]$$

$$III \qquad\qquad\qquad\qquad IV$$

$$\overset{O}{Co}-CH_2-CH_2-CH_2-CH_3 \underset{}{\overset{CH_2=CH-CH_2CH_3}{\rightleftharpoons}} \overset{O}{Co}-H \longrightarrow \overset{O}{Co}-H + CH_2=CHCH_2CH_3$$

$$IV$$

$$[4]$$

$$\overset{O}{Co}-\overset{CH_3}{\underset{}{CH}}-CH_2CH_3 \rightleftharpoons \overset{CH_3CH=CH-CH_3}{\overset{O}{Co}-H} \rightleftharpoons \overset{O}{Co}-H + CH_3CH=CH-CH_3$$

$$V$$

$$IV + C_2H_4 \underset{}{\overset{CH_2=CH_2}{\rightleftharpoons}} \overset{O}{Co}-C_4H_9 \longrightarrow \overset{O}{Co}-CH_2CH_2CH_2CH_2CH_2CH_3 \qquad [5]$$

$$VI$$

$$VI \rightleftharpoons \overset{CH_2=CH-CH_2CH_2CH_2CH_3}{\overset{O}{Co}-H} \rightleftharpoons \overset{O}{Co}-H + H_2C=CHCH_2CH_2CH_2CH_3$$

$$[6]$$

$$\overset{O}{Co}-\overset{CH_3}{\underset{}{CH}}-CH_2-CH_2-CH_2-CH_3 \rightleftharpoons \overset{CH_3CH=CH-CH_2CH_2CH_3}{\overset{O}{Co}-H} \rightleftharpoons \overset{O}{Co}-H + CH_3CH=CHCH_2CH_2CH_3$$

$$VII$$

$$V + C_2H_4 \rightleftharpoons \overset{CH_2=CH_2}{\overset{O}{Co}-\underset{CH_3}{\underset{}{CH}}-CH_2CH_3} \longrightarrow \overset{O}{Co}-CH_2CH_2\underset{CH_3}{\underset{}{CH}}-CH_2CH_3 \qquad [7]$$

$$\downarrow$$

3-Methylpentene-1

$$\overset{O}{Co}-CH_2CH_3 + CH_2=CH-CH_2CH_3 \rightleftharpoons \overset{CH_2=CH-CH_2CH_3}{\overset{O}{Co}-CH_2CH_3} \longrightarrow \overset{O}{Co}-\overset{\underset{CH_2}{\overset{CH_3}{|}}}{\underset{}{CH}}-CH_2CH_2CH_3$$

$$III \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad VIII$$

$$+ \qquad [8]$$

$$\overset{O}{Co}-CH_2-\overset{\underset{CH_2}{\overset{CH_3}{|}}}{\underset{}{CH}}-CH_2CH_3$$

$$IX$$

$$\text{VIII} \rightleftharpoons \underset{\overset{\displaystyle \Big\Updownarrow}{}}{\underset{\text{Co—H}}{\overset{\text{CH}_3\text{CH}\overset{\text{O}}{=}\text{CH—C}_3\text{H}_7}{}}} + \underset{\overset{\displaystyle \Big\Updownarrow}{}}{\underset{\text{Co—H}}{\overset{\text{CH}_3\text{CH}_2\text{CH}\overset{\text{O}}{=}\text{CHCH}_2\text{CH}_3}{}}} \qquad [9]$$

$$\text{Hexene-2} + \overset{\text{O}}{\text{Co—H}} \qquad\qquad \text{Hexene-3} + \overset{\text{O}}{\text{Co—H}}$$

$$\text{IX} \rightleftharpoons \underset{\text{Co—H}}{\overset{\text{CH}_2\overset{\text{O}}{=}\text{C}\diagdown^{\text{C}_2\text{H}_5}_{\text{C}_2\text{H}_5}}{}} \rightleftharpoons \overset{\text{O}}{\text{Co—H}} + \text{CH}_2{=}\text{C}\diagup^{\text{C}_2\text{H}_5}_{\diagdown \text{C}_2\text{H}_5} \qquad [10]$$

similar to those previously proposed [(1) ; see also ref. (4) for a discussion of insertion reactions]. This mechanism is detailed below for the case of ethylene oligomerization [Eqs. (2)–(10)]. Sequential insertion of ethylene could occur to form the observed butene-1 and hexene-1 [Eqs. (2)–(6)]. Partial isomerization [Eqs. (1), (4), (6)] could account for the observed butene-2 and hexene-2. The best way to account for the formation of the abnormally large quantities of hexene-3 and for the formation of 3-methylpentenes is by the reinsertion of butene-1 into the ethyl cobalt intermediate [Eqs. (8)–(10)]. Additional amounts of 3-methylpentenes could be formed by ethylene insertion into the *sec*-butylcobalt (V) formed during partial isomerization [Eq. (7)].

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Density Measurements at Low Temperatures

APPLICATIONS

Density measurements with liquid nitrogen may have advantages in some cases:

(a) if a small molecule is needed to penetrate into narrow pores while water is not suitable; i.e., density measurements of water-soluble substances or of substances (like coal), which are not wetted by water;

diameter H_2O molecule: 2.90 Å; diameter N_2 molecule: 3.15 Å;

(b) if the exact volume of a sample with a small surface area is needed at 78°K for adsorption measurements;

(c) if density measurements are to be carried out in a reproducible way without affecting the properties of the sample; fol-