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Formation of Dimeric Products during Steady State Hydrogenation of Ethylene over Cobalt

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During the steady state hydrogenation of ethylene over cobalt, C_4 hydrocarbons are formed. Such C_4 hydrocarbons are not formed from ethylene alone. The relative yield of C_4 products is enhanced by chemisorbed hydrogen; the distribution of C_4 products is a function of the H_2/C_2H_4 ratio in the reactant stream. These results are similar to those found for nickel catalysts but the yield of C_4 products is greater for cobalt than for nickel. Kinetic analysis suggests that both for nickel and cobalt the C_4 hydrocarbons stem from an adsorbed CH_3CH species that undergoes surface reactions analogous to disproportionation and combination.

INTRODUCTION

Kinetic studies of olefin hydrogenation and exchange over metals suggest that such reactions proceed via an adsorbed ethyl radical (I) (*1–5*). Infrared studies (*6–8*) of adsorbed species formed by ethylene chemisorption on metals and its interaction with hydrogen do provide support for the existence of (I) but these studies also reveal one or more species with trisubstituted CH groups as well as C_4 hydrocarbons. Hydrogen treatment of these residues produces C_4 hydrocarbons (*9*) but published evidence suggests that species other than (I) function substantially as inert residues during steady state hydrogenation.

Recently, (*10*) it has been shown that during the steady state hydrogenation of ethylene over unsupported nickel, C_4 hydrocarbons are produced. Such reactions are not completely unexpected for it has been found that adsorbed ethyl radicals in the presence of hydrogen atoms yield not only ethane but also sizeable amounts of dimer (*11*). Furthermore, transition metal complexes catalyze dimerization of ethylene via the formation of an ethyl radical ligand (*12*). Over reduced nickel, however, the kinds of C_4 products produced competitively with ethane seemed to require reactive intermediates other than adsorbed ethyl radical. Accordingly, it has been suggested (*10*) that a reactive species, CH_3CH (II) is responsible for at least some of the products observed. Such a species has been suggested by Little (*8*) in connection with infrared studies and Eley (*4*) has suggested that such a species may be important at high ethylene coverages. This evidence, however, is not compelling; indeed, intensity data suggest that this species cannot be the sole source of the trisubstituted CH groups observed in infrared studies.

In this paper we extend the study of dimer formation over metal catalysts to cobalt. Comparisons of these data with data previously reported for nickel (*10*) suggest a pattern of reactivity varying primarily in degree rather than kind from one metal to another.

EXPERIMENTAL

Cobalt catalysts were prepared by reduction of the oxide prepared as follows: About 140 ml of 29.7% NH_3 was added to a hot (70–80°C) stirred solution containing 290 g of $Co(NO_3)_2 \cdot 9H_2O$ per liter of water. The blue precipitate was washed repeatedly with 3 liters of hot 0.3% NH_3

and filtered. This solid was air-dried at 125°C, degassed in vacuum for 16 hr at 125°C, and then further degassed for 1 hr at 300°C.

For reduction, the temperature of the catalyst was gradually increased in a stream of tank hydrogen until water appeared (at about 200–225°C) in the exit tube. Reduction was continued at this temperature for several hours at an SVH of about 5000. When water evolution was no longer evident, the temperature was increased to 350°C and reduction was continued overnight. After this the catalyst was regarded as reduced and was cooled in hydrogen for the first sequence of experiments. Prior to each later sequence, the catalyst was purged at room temperature with a hydrogen stream purified by passage through charcoal at —195°C and rereduced in this stream at 325°C for about 2½ hr. The catalyst was either degassed for 1 hr at 325°C or cooled in hydrogen. (The results were the same whether the hydrogen used for reduction was purified by passage over charcoal or not). Surface area and adsorptive properties for such catalysts have been reported (*13*).

Details of the procedure are similar to those reported earlier (*10*). Most runs were made at 25°C with an ethylene flow of 6 to 7 cc/min and hydrogen–olefin ratios varying from 2 to 0. Under these conditions, reaction was complete insofar as when H_2:C_2H_4 was greater than unity, no unreacted olefin was found in the effluent, and when H_2:C_2H_4 has less than unity no unreacted hydrogen was found in the effluent. Dimeric products were *not* observed when pure ethylene was the reactant. All reported yields were those obtained after the catalyst had established a steady state.

RESULTS

Figure 1 shows the overall yield of dimeric products relative to ethane as a function of reactant composition. The upper curve represents data for a catalyst cooled in hydrogen; presumably this catalyst contains chemisorbed hydrogen. The dashed line represents results obtained in the second sequence, prior to which the catalyst was rereduced, evacuated at the reduction temperature, and cooled *in vacuo*; hence, data for this run were presumably obtained on a catalyst without chemisorbed hydrogen. The single solid point was obtained in a third sequence prior to which the catalyst was again rereduced and cooled in hydrogen; hence, this point provides a gauge of the reproducibility of results from one sequence to another.

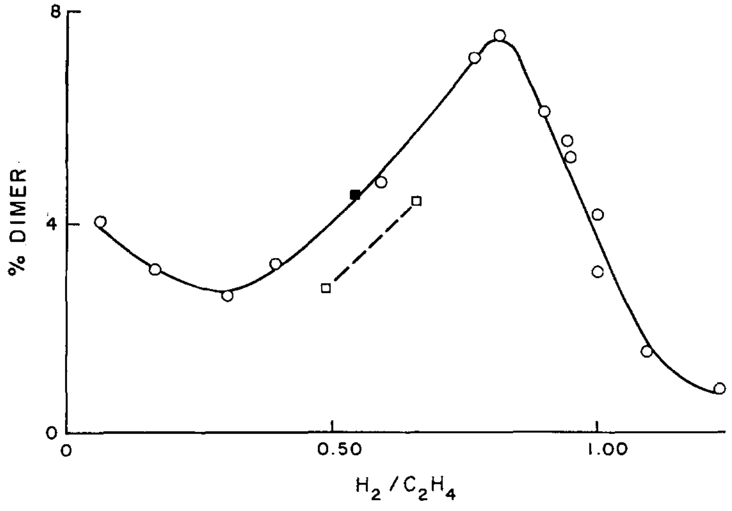

FIG. 1. Total yield of C_4 dimer relative to ethane during the steady state hydrogenation of ethylene over cobalt as a function of reactant composition: ○, Sequence 1, catalyst cooled in hydrogen; □, Sequence 2, catalyst cooled *in vacuo*; ■, Sequence 3, catalyst cooled in hydrogen.

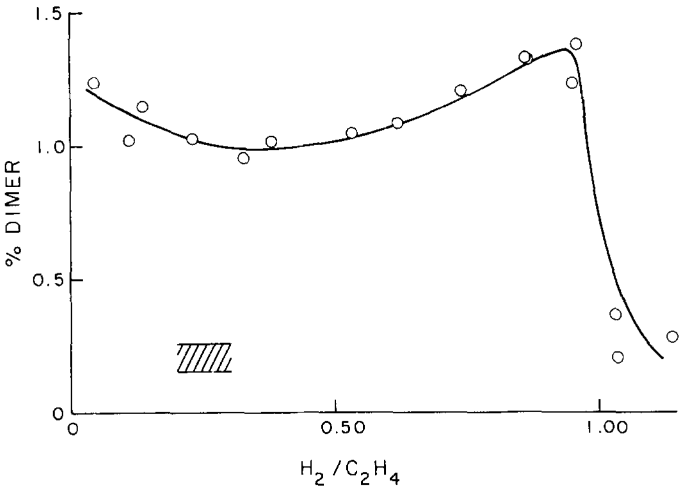

FIG. 2. Total yield of C_4 dimer relative to ethane during the steady state hydrogenation of ethylene over nickel as a function of reactant composition. Points show results for a catalyst cooled in hydrogen; the cross-hatched segment shows the spread for several runs with a catalyst cooled *in vacuo*. [These results were calculated from data reported in ref. (*10*).]

For comparison, we have recalculated the data in ref. (*10*) on the same basis as in Fig. 1 and these data, for nickel, are shown in Fig. 2. The results for nickel and cobalt show the following similarities:

(a) Both curves are similar in shape. As one passes from $H_2:C_2H_4 = 1$ to lower values, there is a steep rise to a maximum. This is followed by a minimum so that there is a nonzero intercept on the ordinate.

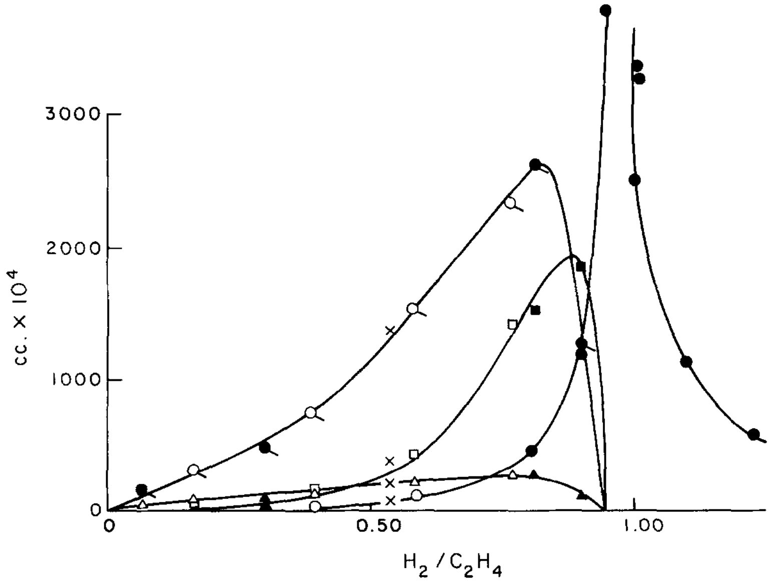

FIG. 3. Amounts of C_4 products/8 cc of effluent during the steady state hydrogenation of ethylene over cobalt as a function of reactant composition. Open symbols are for decreasing H_2/C_2H_4 ratio; closed symbols are for increasing H_2/C_2H_4 ratio; ○, ●, C_4H_{10}; ○, ●, *cis*-2-C_4H_8; □, ■, *trans*-2-C_4H_8; △, ▲, 1-C_4H_8; ×, check points, Sequence 3.

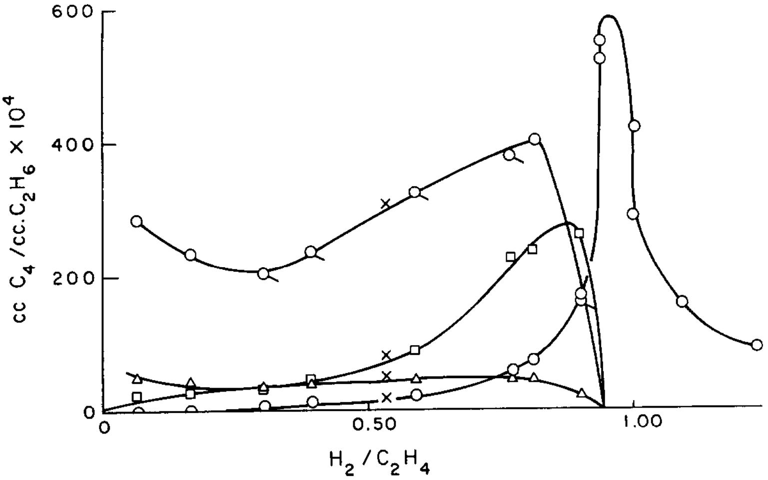

FIG. 4. Ratio of dimeric products to ethane over cobalt as a function of reactant composition: ○, C_4H_{10}; ○, *cis*-C_4H_8-2; □, *trans*-C_4H_8-2; △, C_4H_8-1; ×, check points (Sequence 3).

(b) The relative yield of dimer to ethane is enhanced by the presence of chemisorbed hydrogen. The results for nickel and cobalt show the following differences:

(i) Although the maximum and minimum are apparent in both Fig. 1 and Fig. 2 they are more pronounced for cobalt than for nickel.

(ii) The yield of dimer for cobalt (compared to nickel) is a factor of 5 greater for catalysts with chemisorbed hydrogen and roughly a factor of 25 greater for catalysts without chemisorbed hydrogen.

(iii) The promotion effect of chemisorbed hydrogen is much more dramatic for nickel than for cobalt. For nickel, chemisorbed

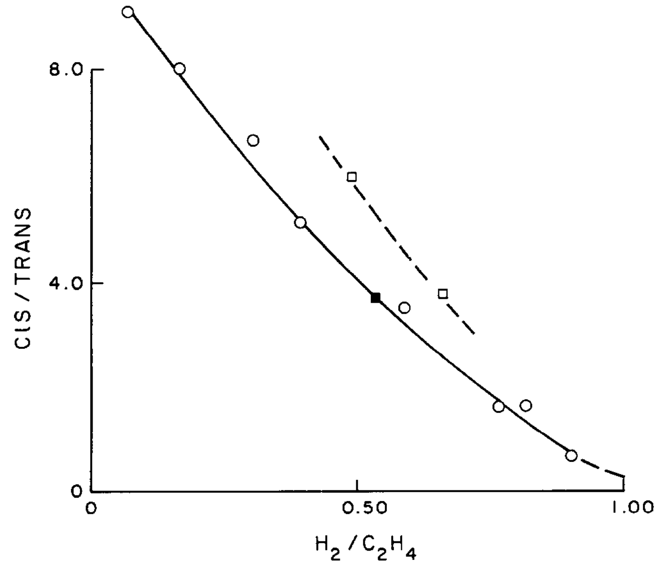

FIG. 5. Ratio of *cis*- to *trans*-butene formed during hydrogenation of ethylene over cobalt as a function of reactant composition: ○, Sequence 1, catalyst cooled in hydrogen; □, Sequence 2, catalyst cooled *in vacuo*; ■, Sequence 3, catalyst cooled in hydrogen.

hydrogen raises the yield by a factor of 5; for cobalt, chemisorbed hydrogen raises the yield by a factor of 1.4.

Figure 3 shows the distribution of products in the effluent stream. The study was initiated in the hydrogen-rich region. Open circles represent points obtained by decreasing the $H_2:C_2H_4$ ratio to zero. The yield of dimeric product was less than 5×10^{-4} cc in the absence of hydrogen, i.e., essentially zero. Solid points were obtained after exposure to pure ethylene. To obtain all of these points which represent steady state values, the catalyst was on stream for 32 hr. Three aspects of the results merit special comment:

(1) The point at $H_2:C_2H_4 = 0.81$ represents values in which the catalyst was on stream at that reactant composition for 15 hr. During this period, the total yield of ethane was about 5200 cc, and the total yield of dimer was about 400 cc. Such large total yields of products relative to the available surface ($V_m \approx 1$ cc STP), clearly indicate catalysis rather than reaction with the surface. Moreover, the agreement of this "long-time" point with adjacent points is strong evidence that we are dealing with steady state catalysis. Further evidence that this is the case is that two points for $H_2:C_2H_4 = 0.95$ taken at $t = 3$ hr and $t = 26$ hr (with intervening variation in reactant composition) differed in product yield by less than 2%.

(2) As shown in Fig. 3, a check point on this catalyst after several rereductions (with intervening runs) yielded essentially identical results; hence, the product distribution, like the overall product yield, is not a sensitive function of the history of the catalyst.

(3) For cobalt, the products also contained polymeric hydrocarbons in higher amounts than was found over nickel. No detailed study was made but it was estimated that as much as 1% of the product were C_6 hydrocarbons.

Figure 4 shows the production of dimer relative to the production of ethane as a function of the $H_2:C_2H_4$ ratio. It is evident that *cis*-butene and 1-butene compete effectively with ethylene for the hydrogen as the $H_2:C_2H_4$ ratio approaches zero, whereas butane and *trans*-butene do not. Similar behavior was found for nickel but, as noted earlier, the yields are much greater for cobalt.

Figure 5 shows the variation of the ratio of *cis*- to *trans*-butene with product composition. The ratio aproaches a value of about 10 for $H_2:C_2H_4 = 0$ for the catalyst cooled in hydrogen. The values for this ratio are lower by a factor of 2 than those for nickel. Furthermore, whereas for nickel the value of this ratio was increased by the presence of chemisorbed hydrogen, for cobalt the value of this ratio was decreased by the presence of chemisorbed hydrogen.

Finally, a few runs were made at $H_2:C_2H_4 = 0.5$ and 125°C. The yields increased with increasing temperature but not as much as previously reported for nickel (*10*), i.e., 50% for cobalt vs a factor of 10 for nickel (*10*). Accompanying this change there was an increase in the *cis/trans* yield from 3.7 to 5.0.

Discussion

The fact that cobalt produces higher dimer yields than nickel suggests that the stability of reactive hydrogen-poor species (which lead to butene formation) is greater over cobalt than nickel. A similar conclusion was reached by Phillipson and Wells (*14*), who found that cobalt isomerized 1-butene in the absence of hydrogen, and postulated a mechanism involving an adsorbed C_4H_7 species. By way of contrast, unsupported nickel (*2*, *10*), as well as unsupported osmium, iridium, and platinum, (*15*) are not effective for butene isomerization in the absence of hydrogen. The effect of chemisorbed hydrogen is smaller for cobalt than for nickel (compare Figs. 1 and 2) but in both cases it acts in the same direction, i.e., it promotes dimer formation. Hall and Hassell (*16*) have noted that ethylene hydrogenation over cobalt and nickel is inhibited by chemisorbed hydrogen. Apparently, then, the ethane formation is inhibited more by chemisorbed hydrogen than dimer formation and this leads to the increase in relative dimer yield in the presence of chemisorbed hydrogen. The fact that chemisorbed hydrogen has a greater effect on nickel than cobalt is also suggested by the data of Hall and Hassell (*16*).

Chemisorbed hydrogen increases the *cis–trans* ratio for nickel (*10*) and decreases it for cobalt. This difference may be a consequence of the operation of different isomerization mechanisms on these metals (*2, 14*).

Differences for cobalt and nickel could arise from bulk structural differences; under the conditions of these experiments, cobalt has a hexagonal close-packed structure (*17, 18*), whereas nickel has a cubic close-packed structure. In our view, however, the differences are in degree rather than kind.* Accordingly, we believe that the same mechanisms operate both for nickel and cobalt and the differences stem from differences in rate constants.

In an earlier paper (*10*) it was shown that the results for nickel seemed to require the presence of a reactive 1,1-diadsorbed species CH_3CH (II). A reaction sequence was presented in outline form that seemed capable of explaining the qualitative features of these results. Since the phenomenon, i.e., selective formation of dimeric products during hydrogenation, seems to be general, it is worthwhile to consider more carefully the experimental consequences of such a sequence in terms of the data presented in Fig. 4.

The sequence discussed earlier (*10*) is summarized (in greater detail) below:

$$(H_2) + 2^* \rightleftarrows 2H^* \qquad (1)$$

$$(C_2H_4) + 2^* \rightleftarrows CH_2CH_2^{**} \qquad (2)$$

$$CH_2CH_2^{**} + H^* \rightleftarrows \underset{(I)}{CH_3CH_2^*} + 2^* \qquad (3)$$

$$CH_3CH_2^* + H^* \rightarrow (CH_3CH_3) + 2^* \qquad (4)$$

$$CH_3CH_2^* + 2^* \rightarrow \underset{(II)}{CH_3CH^{**}} + H^* \qquad (5)$$

$$CH_3CH^{**} \rightarrow CH_2CH_2^{**} \qquad (6)$$

$$2CH_3CH^{**} \rightarrow cis^{**} + 2^* \qquad (7)$$

$$cis^{**} + H^* \rightleftarrows sec^* + 2^* \qquad (8)$$

$$sec^* + H^* \rightarrow (C_4H_{10}) + 2^* \qquad (9)$$

$$sec^* + 2^* \rightleftarrows trans^{**} + H^* \qquad (10)$$

$$CH_3CH_2^* + CH_2CH_2^{**} \rightarrow pri^* + 2^* \qquad (11)$$

$$pri^* + {}^{**} \rightleftarrows bu\text{-}1^{**} + H^* \qquad (12)$$

$$pri^* + H^* \rightarrow (C_4H_{10}) + 2^* \qquad (13)$$

$$bu\text{-}1^{**} \rightarrow (1\text{-}C_4H_8) + 2^* \qquad (14)$$

$$cis^{**} \rightarrow (cis\text{-}C_4H_8) + 2^* \qquad (15)$$

$$trans^{**} \rightarrow (trans\text{-}C_4H_8) + 2^* \qquad (16)$$

The notation is as follows: The symbol * stands for a surface site, e.g., $CH_2CH_2^{**}$ refers to 1,2-diadsorbed ethylene and CH_3CH^{**} refers to the 1,1-diadsorbed isomer; bu-1**, *cis***, *trans*** refer to α,β-diadsorbed C_4 olefins; sec* and pri* refer to monoadsorbed primary and secondary radicals. For clarity, gas-phase species are indicated in parentheses. In order to be specific we have assumed the intermediate CH_3CH^{**} is adsorbed on two sites.

The formation of (II) via (5) merits some comment. It is the same as the reverse of (3) except for the fact that the methylene carbon rather than the methyl carbon loses the hydrogen. It is then assumed that (II) can either isomerize to form adsorbed ethylene (6) or dimerize to form adsorbed *cis*-butene (7). [The reasons for selective formation of *cis*-butene have been summarized in ref. (*10*).] Step (11), or its equivalent, is commonly proposed as a step in the dimerization of ethylene by homogeneous catalysts (*12*). The other steps are the traditional ones listed for reactions of olefins over metals (*5*) except that no pathway has been considered for double-bond migration since this reaction contributes little to the products over nickel (*10*).

First consider the formation of ethane

$$d(C_2H_6)/dt = k_4(CH_3CH_2^*)(H^*)$$

There is abundant evidence (*1*) that step (4) is slow relative to step (3) and its reverse; hence, it is reasonable to assume that equilibrium is maintained for step (3). Therefore

$$d(C_2H_6)/dt = k_4K_3[(CH_2CH_2^{**})(H^*)^2/(^*)^2]$$

If we assume step (1) is also an equilibrium step, we can write

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* It might be argued that one would predict these differences in dimer production on the basis that cobalt is a more effective Fischer-Tropsch catalyst than nickel. However, except for poisoning effects, supported nickel can be an effective Fischer-Tropsch catalyst (*19*). In this connection, however, the observation of Eidus *et al.* (*20*) that an ethylene-hydrogen feed over a cobalt catalyst previously used for synthesis leads to synthesis of higher hydrocarbons is suggestive of the results reported herein.

$$d(C_2H_6)/dt = k_4K_3K_1(CH_2CH_2^{**})(H_2) \quad (17)$$

In the limiting case where the surface is nearly saturated with ethylene, this expression would lead to a rate first order in hydrogen and zero order in ethylene, kinetics often approximated by metal catalysts.

Two assumptions are necessary before kinetic analysis is feasible.* Accordingly, we assume

(a) The steady state concentration of (II) is dominated by (5) and (6),

(b) in the hydrogen-poor region, the surface is nearly saturated with ethylene and the gaps in this near-monolayer, i.e., the empty sites, are independent of the hydrogen pressure.

Then, the steady state requirement for surface species leads to an expression for the production of products which is a power series in (H_2). The lead term, which is most important as H_2 goes to zero, can be determined simply by neglecting terms first order in a surface species and first order in (H^*) with respect to terms first order in the same surface species and zero order in (H^*). This yields the following expressions:

$$\frac{d(cis\text{-}C_4H_8)}{dt} = k_7\frac{k_5^2}{k_6^2}K_3^2K_1(CH_2CH_2^{**})^2(^*)^2(H_2) \quad (18)$$

$$\frac{d(trans\text{-}C_4H_8)}{dt} = \frac{k_{10}k_8}{k_{-8}+k_{10}}\frac{k_7}{k_{15}}\frac{k_5^2}{k_6^2} \times K_3^2K_1^{3/2}(CH_2CH_2^{**})^2(^*)^3(H_2)^{3/2} \quad (19)$$

$$\frac{d(1\text{-}C_4H_8)}{dt} = k_{11}(CH_2CH_2^{**})^2K_3\frac{K_1^{1/2}(H_2)^{1/2}}{(^*)} \quad (20)$$

$$\frac{d(C_4H_{10})}{dt} = \frac{k_{13}(H^*)}{k_{12}(^*)^2}\frac{d(1\text{-}C_4H_8)}{dt} \quad (21)$$

Yields of the above products were obtained in a flow reactor in which the hydrogen was totally consumed. Consider a reaction that is xth order in hydrogen with the rate expression

$$dn_i/dt = k_iw(P_{H_2})^x$$

where n_i represents the moles of product i and w is the weight of catalyst. The yield in a flow system is given by the following equation:

$$n_i^e = k_i\frac{w}{V_0}\frac{n_B^0}{F^0}\int_0^{V_0}(P_{H_2})^x\,dV$$

where n_i^e is the moles of the products at the exit per n_B^0 moles of ethylene at the inlet, F^0 is the inlet flow of ethylene in moles per unit time, and V_0 is the volume of the bed. Since butenes are the major C_4 products in the region of interest and hydrogen is not consumed in their production, the variation of P_{H_2} with bed length is determined by the extent of the reaction to form ethane. For this reaction we can write

$$\frac{n_A}{n_A^0} = \exp -\left\{\frac{kwV}{V_0F^0} + \frac{n_A - n_A^0}{n_B^0}\right\}$$

where n_A is the number of moles of hydrogen at position V in the bed and n_A^0 is the number of moles of hydrogen at the inlet. Provided n_A^0/n_B^0 is less than 0.10 the second term in the exponential can be dropped and the following approximation will be valid to about 10%:

$$P_{H_2} = \frac{n_A^0}{n_B^0}\exp -\frac{kwV}{V^0F^0}$$

Accordingly, in this approximation, the general expression for the ratio of product i at the exit to the inlet ethylene (exit ethane) is given by

$$\frac{n_i^e}{n_B^0} = \frac{k_i}{k}\left[\frac{n_A^0}{n_B^0}\right]^{x-1} \times \left\{\int_0^{V_0}\exp -\frac{xkwV}{V_0F^0}\,dV \Big/ \int_0^{V_0}\exp -\frac{kwV}{V_0F^0}\,dV\right\} \quad (22)$$

Consider first the yields, relative to ethane, of *cis*- and *trans*-2-butene. As the ratio of hydrogen to ethylene (n_A^0/n_B^0) goes to zero, *cis*-2-butene [with $x = 1$ according to Eq. (18)] should approach a

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* We have assumed in this treatment only that steps (1) and (3) are essentially equilibrium steps, but similar results would obtain even if equilibrium was not maintained in step (1).

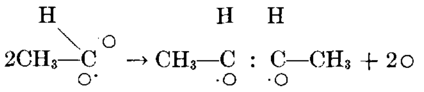
constant value, whereas the yield of *trans*-2-butene [with $x = 3/2$ according to Eq. (19)] should go to zero. This is in accord with results shown in Fig. 4.

The yield of butane can be related to the yield of 1-butene [Eq. (21)]. The factor $k_{13}(\mathrm{H}^*)/k_{12}(*)^2$ (the ratio of hydrogenation to form alkane to alkyl reversal) is small even in a hydrogen-rich reactant mixture and in a hydrogen-poor reactant mixture, the factor will be even smaller; hence, we would expect the yield of butane to be much smaller than the yield of 1-butene. Since the yield, relative to ethane, of 1-butene is quite small, we expect the relative yield of butane to effectively approach zero, as observed.

At first it was believed that dimerization of adsorbed ethyl radicals led to butane. Such a pathway would lead to a rate expression for butane proportional to $(\mathrm{H_2})$. According to Eq. (22) (with $x = 1$) this would lead to a nonzero value in the limit $(n_\mathrm{A}{}^0/n_\mathrm{B}{}^0) = 0$. Since this is not consistent with the data (Fig. 4), we must reject this as an important pathway to butane.

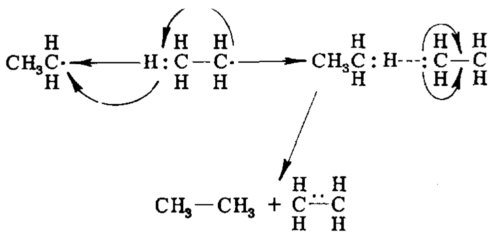
For 1-butene formation [Eq. (20)] $x = 1/2$; hence, the relative yield of 1-butene should increase as $n_\mathrm{A}{}^0/n_\mathrm{B}{}^0$ goes to zero. Instead of this, however, the relative yield of 1-butene increases only slightly; in fact, the shape of the curve for 1-butene is much like that for *cis*-2-butene (Fig. 4). [Results of this analysis were correctly stated in ref. (*10*) but, there, the nonzero intercept for 1-butene and *cis*-2-butene was stressed rather than the shape of the curves.] In this one respect, then, the proposed scheme is unsatisfactory. Accordingly, let us look for an alternative pathway to 1-butene. To do so, let us accept the proposed scheme except for the step leading to 1-butene.

In the gas phase, ethyl radicals dimerize to form butane or disproportionate to form ethane plus ethylene (*21*, *22*). When an ethyl radical forms one bond to a surface metal atom, however, the accompanying stabilization is sufficient to inhibit these reactions; as a consequence, no butane is formed *via* the bimolecular reaction of adsorbed ethyl radicals. By way of contrast, when two surface bonds are formed to a given carbon atom, some radical character is retained insofar as reaction (7) can be viewed as the dimerization reaction for a substituted radical. To emphasize this similarity let us rewrite reaction (7) as follows:

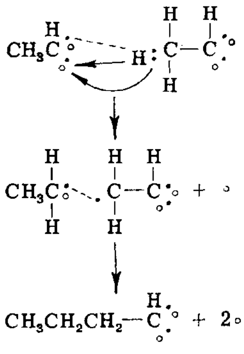


$$2\mathrm{CH_3}{-}\overset{\mathrm{H}\ \ \circ}{\underset{\circ\cdot}{\mathrm{C}}} \rightarrow \mathrm{CH_3}{-}\overset{\mathrm{H}}{\underset{\cdot\circ}{\mathrm{C}}} : \overset{\mathrm{H}}{\underset{\cdot\circ}{\mathrm{C}}}{-}\mathrm{CH_3} + 2\circ$$

wherein the symbol ○ represents the electron from the metal in the carbon surface bond. What then would be the analog to disproportionation? Isotopic studies in the gas phase (*21, 22*), show that disproportionation occurs by transfer of a methyl hydrogen from one radical to another. It is suggested that this involves a head-to-tail encounter* that can be pictorially represented by



Such a sequence, with significant ionic contributions to the transition complex, is consistent with many of the details of radical reaction kinetics. We can pictorially represent a similar surface encounter as follows:



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* Alternative interpretations of isotopic experiments involve ring formation in the activated complex (*21*). Such a pathway for the surface reaction would lead to similar conclusions but steric requirements are somewhat excessive.

[This sequence can also be viewed as the analog of a carbene insertion reaction (*23*).] The resulting surface species can rearrange via the equivalent of reaction (6) to form adsorbed 1-butene or it can react further with the CH_3-CH species to give rise to the C_6 hydrocarbons found in the products. Thus, if for reaction (11) we substitute

$$2CH_3\text{—}CH^{**} \rightarrow CH_3\text{—}CH_2\text{—}CH_2\text{—}CH^{**} + 2^{**} \qquad (11')$$

and

$$CH_3\text{—}CH_2\text{—}CH_2\text{—}CH^{**} \rightarrow \text{bu-1}^{**} \qquad (11'')$$

the yield of 1-butene would have the same limiting functional dependence on $n_A{}^0/n_B{}^0$ as the yield of *cis*-2-butene, in line with the experimental observations (Fig. 4).

In conclusion, then, it appears that an adsorbed ethyl radical on a metal is so much stabilized that it does not undergo radical-type reactions, i.e., dimerization or disproportionation. There does exist a species, however, that does yield C_4 products. It is proposed that this species is an α,α-diadsorbed C_2 species that retains radical reactivity and undergoes the analog of disproportionation and combination to yield initially 1-butene and *cis*-2-butene, respectively, and that other C_4 products arise from subsequent reactions of the initial products. Evidence for α,α-diadsorbed species on the surface is somewhat sketchy (*10*) but recent X-ray studies of transition metal compounds (*24*) have shown that substituted carbenes can bond directly to the metal atom. Such bonds represent the analog of the bonding in (II). It is recognized, of course, that the proposed intermediate and its reactions do not represent a unique interpretation, but this proposal does have the advantage that it seems to be consistent with the facts and involves a species which is at least plausible in view of the existing experimental data.

ACKNOWLEDGMENT

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REFERENCES

1. BOND, G. C., AND WELLS, P. B., *Advan. Catal.* **15,** 91 (1964).

2. TAYLOR, T. I., "Catalysis" (P. H. Emmett, ed.), p. 257, Vol. 5. Reinhold, New York, 1957.

3. SIEGEL, S., *Advan. Catal.* **16,** 123 (1966).

4. ELEY, D. D., "Catalysis" (P. H. Emmett, ed.), p. 49, Vol. 3. Reinhold, New York, 1955.

5. BOND, G. C. "Catalysis by Metals." Academic Press, New York, 1962.

6. EISCHENS, R. P., AND PLISKIN, W. A., *Advan. Catal.* **10,** 1 (1958).

7. SHEPPARD, N., *Pure Appl. Chem.* **4,** 71 (1962).

8. LITTLE, L. H., "Infrared Spectra of Adsorbed Species," p. 100. Academic Press, New York, 1966.

9. MCKEE, D. W., *J. Amer. Chem. Soc.* **84,** 1109 (1962).

10. KOKES, R. J., AND BARTEK, J. P., *J. Catal.* **12,** 72 (1968).

11. INNES, R. B., AND KOKES, R. J., unpublished results.

12. (a) CRAMER, R., *J. Amer. Chem. Soc.* **87,** 4717 (1965); (b) WILKE, G., BOGDONOVIC, B., HAIDT, P., HEINBACH, P., KEIM, W., KRONER, M., OBERKERCH, W., TANAKA, K., STEINRUCKE, E., WALTER, D., AND ZIMMERMAN, H., *Angew. Chem. Intern. Ed. Engl.* **5,** 151 (1966). (c) KELLY, A. D., FISHER, L. P., BERLIN, A. J., MORGAN, C. R., GORMAN, E. H., AND STEADMAN, T. R., *Inorg. Chem.* **6,** 657 (1957).

13. KOKES, R. J., *J. Amer. Chem. Soc.* **82,** 3018 (1960).

14. PHILLIPSON, J. J., AND WELLS, P. W., *Proc. Chem. Soc.*, p. 222 (1964).

15. MELLOR, S. D., AND WELLS, P. B., unpublished results [referred to in Wells, P. B., and Wilson, G. R., *J. Catal.* **9,** 70 (1967)].

16. HALL, W. K., AND HASSELL, J. A., *J. Phys. Chem.* **67,** 636 (1963).

17. HOFER, L. J. E., AND PEEBLES, W. C., *J. Amer. Chem. Soc.* **69,** 893 (1947).

18. JOICE, B. J., ROONEY, J. J., WELLS, P. B., AND WILSON, G. R., *Discuss. Faraday Soc.* **41,** 223 (1966).

19. STORCH, H. H., GOLUMBIC, N., AND ANDERSON, R. B., "The Fischer-Tropsch and Related Synthesis," p. 125. Wiley, New York, 1951.

20. EIDUS, Y. T., results quoted by Gibson, E. J., and Clarke, R. W., *J. Appl. Chem.* **11,** 293 (1961).

21. KERR, J. A., AND TROTMAN-DICKENSON, A. F., *Progr. React. Kinet.* **1,** 113 (1961).

22. Benson, S. W., *Advan. Photochem.* **2**, 1 (1964).
23. DeMore, W. B., and Benson, S. W., *Advan. Photochem.* **2**, 219 (1964).
24. Candlin, J. P., Taylor, K. A., and Thompson, D. T., "Reaction of Transition Metal Complexes," p. 257. Elsevier, Amsterdam, 1968.