

Adsorption and Reaction of Cyclopropane and Hydrogen on Nickel

Changes in Selectivity with Temperature

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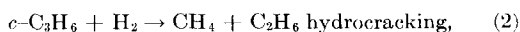
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Received July 27, 1969

A comparative study was made of the cyclopropane chemisorption on pure nickel film surfaces and of the hydrogenation and hydrocracking of cyclopropane on both the films and a reduced nickel catalyst. In a range of higher coverages, the chemisorption of cyclopropane at 273°K was accompanied by selfhydrogenation to propane, and, as a characteristic feature of the process on nickel, cracking to methane and ethane was also observed. Some further data concerning composition and properties of the chemisorbed layers are also given. Cyclopropane was reacted with hydrogen on nickel films in an UHV apparatus at 195 and 273°K, and in the range of 300-600°K using a microcatalytic-pulsed reactor coupled to a gas chromatograph. For the purpose of comparison, hydrocracking of propane was also investigated under the same conditions on the nickel powder catalyst. From the temperature variation of the product composition thus obtained, two types of cyclopropane cracking could be distinguished. With the low-temperature selective hydrocracking, the percentage of methane and ethane in overall product was constant over the range of 195-500°K. Beyond this range the nonspecific hydrocracking began, characterized by the increasing proportion of cracking in products and by the prevalence of methane over ethane. No distinction could be made between the latter process and the propane or propylene hydrocracking. Some mechanistic consequences of the experimental findings are discussed. A concerted simultaneous splitting of two bonds in the chemisorbed cyclopropane ring is suggested as the reaction path for the low-temperature fragmentation.

INTRODUCTION

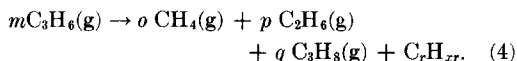
Some of the properties of the cyclopropane molecule are reminiscent of those of unsaturated hydrocarbons such as ethylene or propylene (1, 2). However, we find with cyclopropane some features not observed with those unsaturates, e.g., its molecule is easily split at low temperature (0°C). With hydrogen, cyclopropane undergoes reactions of the following stoichiometry:



The relative participation of each particular reaction in the overall conversion of cyclopropane depends on temperature and the metal used. This renders the molecule of cyclopropane attractive for the studies of selectivity patterns of metals.

As previously shown (3-5), in the course of cyclopropane chemisorption (no hydrogen added to the gas phase) the following products are formed on the metal surface according to the overall stoichiometric equation

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The relative participation of reaction (2) in the overall catalytic process is higher on those metals, having also higher the ratio $(o+p)/q$ or $(o+p)/m$ in chemisorption [o, p, m, q—according to Eq. (4)]. The main body of results (3–5) has hitherto been obtained at one temperature only. The present paper reports extended data for nickel and results on the temperature dependence of the catalytic reaction.

EXPERIMENTAL METHODS

As with other metals (4, 5), chemisorption of cyclopropane on nickel films was studied in an UHV apparatus (6). Analysis was performed by means of a mass spectrometer, directly connected with the adsorption system. Using the same apparatus, the composition of products of catalytic conversion by films at 195 and 273°K was determined under static conditions.

At higher temperatures, the composition of products of hydrogenation and hydrocracking was determined employing the chromatographic pulse reactor technique (7). In these experiments electrolytic hydrogen streamed through a trap (liquid N₂), desoxocatalyst (Pd on SiO₂, 20°C) and the

second trap filled with molecular sieve (Linde, 13X) to the reference cell. Then it passed a catalytic reactor, chromatographic column, and through the detector cell left the apparatus. Cyclopropane (or any other gas) was injected through a rubber septum-sealed injection port placed close to the reactor.

Cyclopropane (ICI, medical grade), propylene, propane, methane, and ethane (Matheson Co., c.p. grade) were used for the study of reactions and for calibration purposes. Catalytic conversion was studied with slugs of cyclopropane of 0.25–0.45 ml (NTP), the flow rate of gases 50 ml/min and barometric pressure. The detection was katharometric; the peak areas, proportional to the number of molecules (injected or produced), were determined by planimeter. The chromatographic column (70-cm long, 6-mm diam) was packed with Poropak Q (Waters Associates Inc., 50–80 mesh) and kept at 80°C—at lower temperatures the memory effect was too high. The catalyst was placed in the reactor tube forming a layer about 10-mm thick, held in place by a plug of glass wool. The weight of catalyst was 1 g. Nickel was prepared, in these experiments, from nickel oxide by reduction *in situ* at 450°C (8-hr reduction was used). After an interruption of experiments when

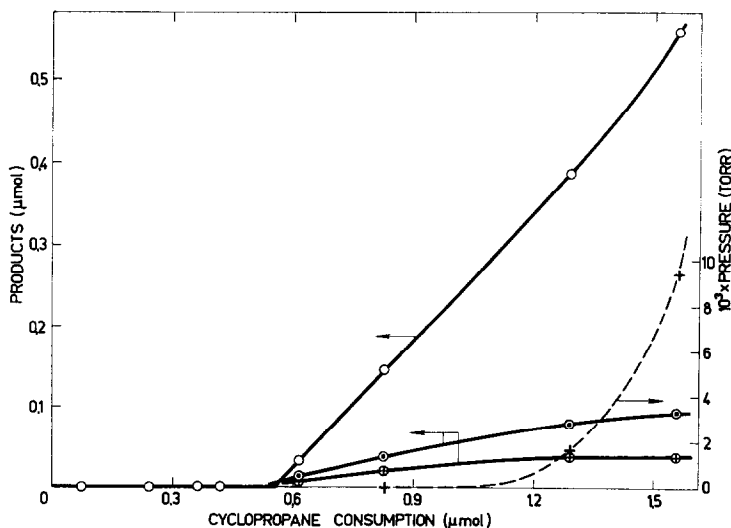


FIG. 1. Chemisorption and disproportionation of cyclopropane on nickel film (273°K). Products: propane, ○; ethane, ⊙; methane, ⊕. Pressures of cyclopropane established in the individual doses; +.

repeating the measurements on another day, etc., the same reduction treatment was always applied. Both data, for the "fresh" and "regenerated" catalyst, are plotted in the following graphs.

RESULTS

The selfhydrogenation on nickel has the same characteristic features as with other metals (4) (Fig. 1). When a certain consumption q^* of cyclopropane by the surface is reached (this point is quite sharply defined), gaseous products of disproportionation reaction (4) appear in the apparatus. The value of the ratio m/q [Eq. (4)] is approximately 2, as with other metals (4, 5).

As mentioned already in our earlier paper (4) the ratio H/C for the adsorbed phase can be calculated on the basis of analysis of the gas phase. When the maximum consumption of cyclopropane was reached at the coverage q_{tot} (in two experiments $q_{\text{tot}} = 1.67$ and $1.82 q^*$, respectively—here q^* and q_{tot} are expressed in the numbers of surface C-atoms) the ratio H/C in the adsorbed phase was 1.49 and 1.46, respectively. However, part of the hydrogen atoms were split from the chemisorbed hy-

drocarbon species and could be displaced to the gas phase by means of carbon monoxide. Upon desorption of all displaceable hydrogen (and traces of hydrocarbons) the apparent ratio H/C dropped down to 1.17 (4).

The chemisorbed layer of the extent q_{tot} could be hydrogenated. Approximately 77% of originally present C-atoms were released as gaseous products in this way. The presence of C_4 and higher hydrocarbons in the gas phase after hydrogenation showed that, in addition to the reaction of cleaving, also the reconstitution of C-C bonds (recombination, or "polymerization") had taken place in the adsorbed phase, already at 273°K . [The mechanism of displacement and polymerization was discussed in Ref. (4)]. In contrast to this, no higher hydrocarbons were detected after the catalytic conversion of a mixture of cyclopropane and hydrogen.

For an easier presentation of results concerning the catalytic reaction, following quantities have been introduced, viz, total consumption n_{Δ}^{cons} , overall conversion C (%); proportion of cracking in conversion C_c (%); proportion of nonselective cracking [reaction (3)] in the total cracking N_c .

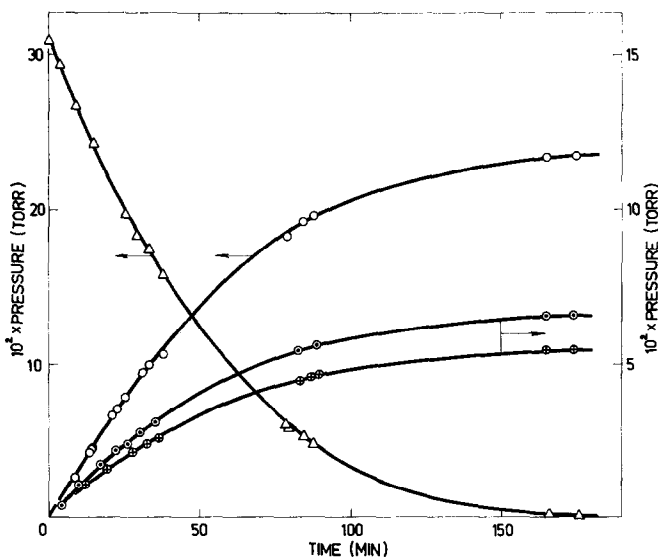


FIG. 2. Hydrogenation of cyclopropane on nickel film (273°K). Time course of partial pressures of: cyclopropane, Δ ; propane, \circ ; methane, \oplus ; and ethane, \odot . Initial hydrogen pressure 4.0×10^{-1} Torr. The same film as in Fig. 1 was used after hydrogenation of the removable part of chemisorbed layer.

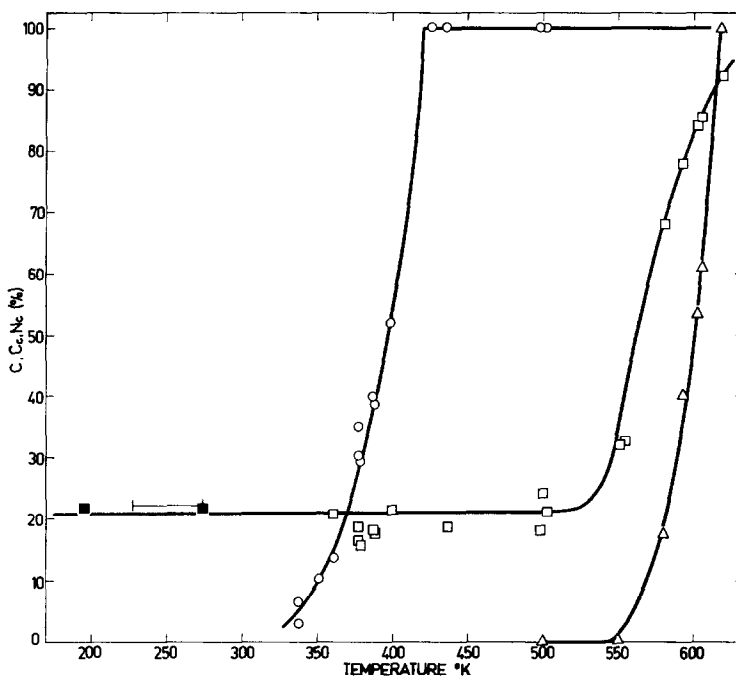


FIG. 3. The variation of selectivity in cyclopropane hydrogenation and hydrocracking with temperature. The values of overall conversion C , \circ ; proportion of cracking in conversion C_e , \square ; and proportion of non-selective cracking in total cracking N_c , \triangle ; obtained after passage of a cyclopropane slug through the nickel powder bed. Results for evaporated films (\blacksquare), and from Ref. (8) (—) are also included.

(%). Symbol n indicates the number of molecules, consumed or produced, the lower index specifies the molecule (Me = methane, Ea = ethane, Pa = propane, Δ -cyclopropane). Mass balance can be formulated according to the reactions (1), (2), (3) (each one corresponds to one member of the following sum):

$$n_{\Delta}^{\text{cons}} = n_{\text{Pa}} + n_{\text{Ea}} + \frac{1}{3}(n_{\text{Me}} - n_{\text{Ea}}).$$

Hence,

$$C = 100 n_{\Delta}^{\text{cons}} \cdot (n_{\Delta}^{\text{injected}})^{-1} (\%),$$

$$C_e = [n_{\text{Ea}} + \frac{1}{3}(n_{\text{Me}} - n_{\text{Ea}})] \cdot (n_{\Delta}^{\text{cons}})^{-1} \cdot 100 (\%),$$

$$N_c = \frac{1}{3}(n_{\text{Me}} - n_{\text{Ea}}) \cdot [n_{\text{Ea}} + \frac{1}{3}(n_{\text{Me}} - n_{\text{Ea}})]^{-1} \cdot 100 (\%),$$

The time course of a reaction over a nickel film in the static apparatus is shown in Fig. 2.

The data obtained by the chromatographic technique with powdered nickel are collected in Fig. 3. At temperatures round 420°K all injected cyclopropane is already converted to products (under conditions

used here). With all conditions kept constant (the same catalyst, amount of cyclopropane injected, time of contact) the proportion of cracking C_e remains constant up to the temperature of 520°K. At higher temperatures cracking is stronger and the proportion of methane in products increases. The Arrhenius plot of $\log C$ (%) vs. $1/T$ is linear over 340–400°K range and the apparent activation energy is 9 kcal/mole. In the same Fig. 3 the data are also plotted from the paper by Anderson and Avery (8). Those data were obtained in a conventional vacuum apparatus with nickel films. Furthermore, our own results, obtained with films under static conditions in an UHV apparatus, are also shown.

One point concerning the determination of n_{Ea} (and also all parameters derived from n_{Ea}) must be mentioned here. At the temperatures when only reaction (2) [and not Eq. (3)] occurred, the value found for n_{Ea} was always slightly higher than that for n_{Me} , in spite of the fact that according

to the stoichiometry of reaction (2) both values should have been equal. We observed this effect using both gas chromatography (with powders) and mass spectrometry (with films). The difference was rather small but it was systematic and seemed to be higher than the estimated error in analysis. It is interesting that a similar deviation can be seen in the results of other authors, too (9, 10). One can suggest that, under conditions of the reaction, some dimerization of C_1 to C_2 species also is possible. However, as no higher hydrocarbons are detected in the reaction mixture, the mechanism of this dimerization must be somehow different from the recombination of surface species in the absence of hydrogen.

DISCUSSION

As evident from Fig. 2, the yield of methane increases with temperature beginning from 520°K. Methane can be produced either directly by reaction (3), prevailing at the higher temperatures over the parallel reaction (2), or by successive cracking of the products of primary reaction (2), i.e., by cracking of propane and ethane. In Fig. 4 the relative degree of overall propane cracking [$C = n_{Pa}^{cons} \cdot (n_{Pa}^{injected})^{-1} \cdot 100$ (%)] and the relative yield of methane [$N = n_{Me} / (n_{Me} + n_{Ea})^{-1} \cdot 100$ (%)] characterizing the deep propane cracking, are shown as a function of temperature. With the other conditions (contact time, partial pressures, catalyst) unchanged, the cracking of propane and the increase in N began at about the same temperature as the increase in deep cracking of cyclopropane. Under these conditions cyclopropane can be converted fully to its hydrogenated products; therefore, the data obtained do not answer the question as to whether the deep cracking of cyclopropane is parallel or successive to reaction (2). However it can be concluded that the latter process is possible.

Figure 2 shows also that the ratio of rates of cyclopropane reactions (1) and (2) changes neither with the slug size in chromatographic experiments, nor in the course of reaction under static conditions with

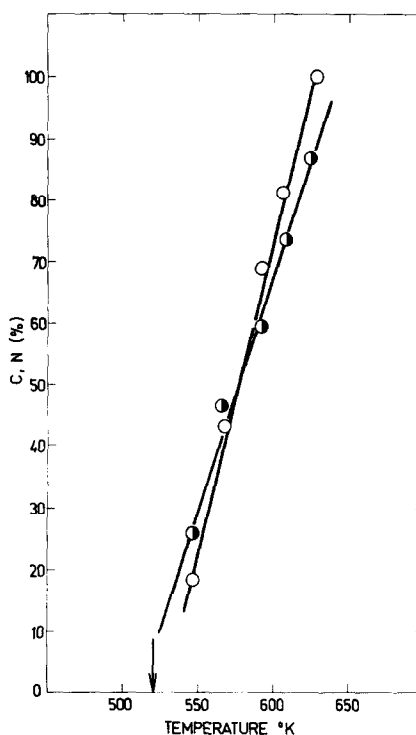


FIG. 4. Temperature variation of products composition after passage of a propane slug through the nickel powder bed: Overall cracking C , ○; and the percentage of methane in product N , ●. The outset of nonspecific cyclopropane hydrocracking is indicated by the arrow.

nickel films. In both cases the partial pressures of reaction components vary, but without any influence on C_c value. The temperature insensitivity of C_c necessarily means that the temperature dependencies of rates of reaction (1) and (2) are the same ones. It is quite improbable that the exponential temperature variation of the rate constants ratio would be just compensated by an inverse temperature dependence of the ratio of concentration terms of respective rate expressions. Rather it is possible to expect the concentration terms temperature dependencies to cancel—the same as their partial pressure dependencies do. Therefore, we are inclined to believe that both reactions have the same activation energy, e.g., given by the activation energy of the step which just dictates the ratio of reactions (1) and (2) in conversion.

The difference between the selective function of metals in cyclopropane reactions (4) and the nonselective behavior in propane cracking (11, 12) shows that the successive decomposition of firmly adsorbed species derived from a propane structure and hydrogenation of C₁ and C₂ species thus formed are not responsible for the low temperature cyclopropane cracking. Likewise, the isomeric propylene is not cracked under the same conditions. This was found earlier (10) and has been confirmed by our work. Therefore, the low-temperature cracking of cyclopropane is inherently tied up with the cyclic structure; the fragmentation to C₂ and C₁ species starts directly from the cyclic structure by simultaneous breaking of two C-C bonds, not passing via particles formed by ring opening. More evidence supporting this mechanism can be found in the results by Proudhomme and Gault (13) (deuteration and exchange of 1,1-dimethylcyclopropane). According to them, there is no difference between the intermediates for ring opening on both nickel and palladium, in spite of the fact that on nickel a specific demethanation was observed. The process of "concerted" opening of the two bonds demands probably sites with proper configuration of surface atoms (14), at least a pair of unoccupied adjacent metal atoms. Figure 1 shows a tendency for preferential cracking at lower surface coverages, where the number of suitable sites (doublet or similar) is naturally higher.

One can also consider direct elimination of a part of chemisorbed cyclopropane molecule (necessarily connected with hydrogen shifts—possibly assisted by surface atoms or neighboring surface complexes) into the gas phase. However, as at coverages less than q^* , both fragments always remain stuck on the surface and do not appear in the gas phase, it is necessary to suppose that both fragments of the cyclopropane molecule react with the metallic surface.

The activation energy derived from the temperature dependence of C_c is 9 kcal/mole. This value obtained under chromatographic regime with powdered nickel is the same as the value found with nickel films in the static apparatus with circula-

tion, at about 10 Torr pressures of equimolar reaction mixture (15). Bond (16) reports the same value for platinum-group metals. The value of 6.5 kcal/mole has been obtained from two reaction runs at about 0.5 Torr pressures of both reactants over nickel films prepared and tested in our UHV apparatus without circulation.

It is remarkable that the selectivity of nickel (see Fig. 3) does not vary with different ways of catalyst preparation. Other authors also found (17) that the specific activity of Pt-catalyst is not sensitive to the catalyst preparation. Apparently reactions of cyclopropane belong to the so-called structure-insensitive (facile) reactions (18, 19), in contrast to the structure-sensitive (demanding) reactions—like isomerizations. This behavior is surprising indeed, because the conversion of cyclopropane can apparently proceed via two alternative pathways, one of them most likely using multiple atom sites [see Ref. (19)].

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