

**PROPERTIES
OF CHEMISORBED HYDROCARBON LAYERS ON METALS. I.
DISPROPORTIONATION
OF CYCLOPROPANE ON IRON**

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Dedicated to the 65th anniversary of the late Academician R. Brdička.

Received June 1st, 1970

The following experimental procedures were used to study the nature and reactivity of particles produced by chemisorption of unsaturated hydrocarbons on metal film surfaces: determination of the course of selfhydrogenation, hydrogenation of chemisorbed layers, displacement of surface particles during adsorption of carbon monoxide, exchange of surface hydrogen by deuterium. A full description of apparatus and those procedures, together with the data obtained by mass-spectrometric analysis, has been given. This has been demonstrated on the results achieved with cyclopropane on iron. It was established that the iron surface dissociated cyclopropane molecules even at 0°C, when no selfhydrogenation was detected. At 50°C, selfhydrogenation accompanied by cracking took place and, as a characteristic feature of the process on iron, a considerable desorption of hydrogen was observed. The maximum extent of adsorption at 0°C appeared identical with the surface coverage that was necessary to produce selfhydrogenation at 50°C. Gaseous cyclopropane was nonreactive towards various forms of preadsorbed hydrogen at 0°C. All these facts could be rationalized on the basis of the selfhydrogenation mechanism in which interactions in the adsorbed layer were decisive. As a slow step in this mechanism, recombination of the C—H bond has been suggested. Likewise, kinetics of the catalytic hydrogenation of cyclopropane were studied; a comparison with the experiments on chemisorption showed that reaction products correspond to the gaseous products of selfhydrogenation, but not all the residues taking part in the hydrogenation of the layer are intermediates in the reaction.

In communication¹, it has been shown on a series of transition metals that the selectivity of the catalytic hydrogenation and hydrocracking of cyclopropane corresponds to the selectivity of selfhydrogenation and cracking during cyclopropane chemisorption. Furthermore, parallelity between the activity of surfaces in the catalytic reaction of cyclopropane with hydrogen, and the reactivity of chemisorbed layers towards hydrogen was observed. This behaviour was in both cases explained by a common mechanism of the interaction of cyclopropane with the surface. This makes it possible to apply knowledge of the layers of chemisorbed complexes in the discussion on the reaction mechanism. Of no less importance is also the information

concerning the nonreacting part of the chemisorbed layer from the viewpoint of its influence on the overall catalytic behaviour of the surface, *e.g.*, selectivity, self-poisoning *etc.* A more extensive account of results achieved on nickel has been published already². This paper presents results on iron in a more detail.

EXPERIMENTAL

Apparatus and Pumping

A bakeable high-vacuum apparatus (Fig. 1) was used for the preparation of pure metallic films and adsorption measurements. Vacuum necessary for vapour-deposition of films was achieved by a procedure suggested by Biondi³, and Pasternak and Wiesendanger⁴. A three-stage fractionating oil diffusion pump operating with Convalex 10 was used⁵. In the high-vacuum part, a molecular sieve trap was included to stop possible back diffusion of oil. To isolate the apparatus from the pump as well as individual parts of the apparatus from each other, bakeable cutoffs filled with an eutectic alloy⁶ consisting of gallium, indium, and tin were used. This alloy has a very low vapour pressure (the most volatile component, indium, attains⁷ 10^{-10} Torr at 400°C) and is liquid at room temperature, which facilitates its good degassing. From several examined alter-

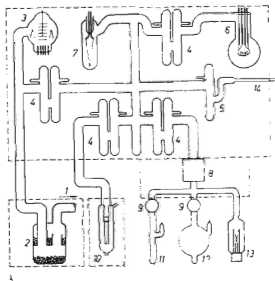


FIG. 1

Diagram of Apparatus

1 To diffusion pump, 2 trap with artificial zeolite, 3 ionization gauge, 4 and 5 alloy cutoff, 6 adsorption vessel, 7 thermal-conductivity vacuum gauge, 8 and 9 metallic valves, 10 palladium tube, 11 reservoir for carbonyl, 12 reservoir for hydrocarbons, 13 auxiliary thermocouple gauge, 14 tube to the ion source of the mass spectrometer. Heated parts of the apparatus are surrounded by dashed lines.

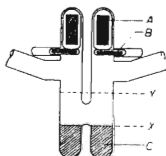


FIG. 2

Construction of the Alloy Cutoff

A Plunger with iron core, B magnetically operated plug, C Ga-In-Sn alloy, X alloy level in the open position, Y alloy level in the closed position.

natives the cutoff illustrated in Fig. 2 proved to be the most advantageous one. It allows to attain overpressures up to 10 Torr, has a relatively high conductivity, and is fairly safe against the alloy overspilling at unexpected bursts-in of air. An all-metal bakeable valve (Edwards High Vacuum Co. Ltd.) was used for admitting gases into the apparatus. The gas reservoirs were closed by valves made by Hoke, Inc.

Before starting the evacuation cycle, the molecular sieve trap was heated at 400°C for 24 hours. Desorbed vapours were pumped into the active charcoal cooled with liquid nitrogen. Thus, without specially degassing the charcoal, pressure of the magnitude order of 10^{-3} Torr could be attained. After that time, heating power of the diffusion pump was switched on, and when a pressure of approximately $5 \cdot 10^{-4}$ Torr with the zeolite still hot had been reached within next few hours, the bakeout of the high-vacuum part of the apparatus was started. After reaching a pressure of approximately $2 \cdot 10^{-4}$ Torr, baking of the zeolite was stopped and the trap was kept at room temperature for the rest of the experiment. Auxiliary experiments showed that cooling the zeolite with liquid nitrogen did not practically affect the achieved limiting vacuum.

The high-vacuum part of the apparatus was heated with an oven inside of which a temperature of 400–450°C could be attained at the stationary state. During degassing the apparatus (with cooled zeolite), electrodes of the ionization gauge and the filament for vapour-deposition were simultaneously heated. This stage lasted for 40–50 hours, depending on previous history of the apparatus and the kind of metal to be evaporated. The items in the high-vacuum part which were not directly closed in the oven could be kept at c. 300°C by means of heating wraps (Pd-tube, gas handling volume), or they were subjected to a multiple degassing by flaming (the inlet tube of the mass spectrometer).

After switching off the heating of the oven and other parts of the apparatus, the pressure decreased down to 10^{-8} Torr during the cooling already. However, degassing of the alloy in the cutoffs, where small amounts of gas remained incorporated, was still needed. These were expelled by thorough mixing of the alloy by means of the plungers until no increase of pressure over the 10^{-8} Torr range occurred in the process. This procedure was particularly important in cases when, e.g., a violent burst-in of air and spillover of the alloy preceded the experiment. According to circumstances, thorough degassing of the cutoffs lasted up to 3 hours. With the cutoffs degassed, the vessel for film deposition was once more heated for a short time. The pressure of $2-20 \times 10^{-10}$ Torr was thus achieved in the cooled apparatus with the ionization gauge cathode and the vapour-deposition filament glowing.

Vapour-Deposition of Films

Before starting the bakeout and the degassing of the apparatus, the iron wires used were reduced with hydrogen *in situ* for 2–4 hours under a pressure of approximately 10 Torr (the filament temperature was about 1000°C). The films were prepared in an usual manner⁸ by direct vapour-deposition from the wires (Reineisen-Vakuumschmelze A. G., Hanau) onto the wall of the adsorption bulb, cooled with liquid nitrogen. The films on which the adsorption measurements were carried out at 0°C were stabilized by heating up to 60°C and left in a bath for 12 hours to cool down to the room temperature. For the experiments at 50°C, the films were kept in a bath having temperature of 70°C for a period of 6 hours.

Measurements of the Film Resistance

The adsorption vessel was furnished with contacts that allowed to measure the film resistance by a procedure described, e.g., by Knor and Ponec⁸. The film resistance was examined even during the deposition, when it served, with regard to the stable geometric arrangement, as an orientational

measure of the chosen film thickness. In addition, the resistance measurement was applied to detect surface processes during chemisorption, catalytic reaction *etc.*, as presented below in the description of the experiments.

Preparation and Purification of Gases

In the adsorption experiments, cyclopropane, hydrogen, deuterium, and carbon monoxide were used. Methane, ethane, and propane were further used for calibrations of the mass spectrometer. *Cyclopropane* was taken from a cylinder (medical grade, ICI, Wilmslow, Cheshire) and supplied to the reservoir, where it was purified by repeated freezing at the liquid nitrogen temperature and pumping. *Hydrogen* was produced by electrolysis of the KOH solution and introduced into the apparatus through a heated Pd tube. *Deuterium* was prepared by electrolysis of heavy water enriched to 99.7%, in which a small amount of calcinated K_2SO_4 was dissolved. The preparation of deuterium of higher purity than 97% was associated with certain difficulties due to kinetic isotope effect occurring during diffusion through the palladium tube. The doses of higher purity were mostly prepared in such a way that a larger amount of gas was introduced, and afterwards, the gas was partly let out back through the hot Pd tube. *Carbon monoxide* was prepared by the decomposition of iron pentacarbonyl. It was important for the desorption experiments that the used carbon monoxide should not contain significant amounts of hydrogen. From the various preparations which could be made directly in the apparatus, decomposition of carbonyl met the above requirement best (less than 0.1% hydrogen was detected). For most of time, the carbonyl was kept frozen at the dry-ice temperature and warmed merely to prepare carbon monoxide by the decomposition on a hot tube wall. The other gases (c.p., Matheson Co.) used for the calibration of the mass spectrometer were taken directly from cylinders.

Pressure Measurements

Adsorption and catalytic reactions were followed by means of pressure changes in known volumes of the apparatus calibrated in advance. For the pressure measurements of pure gases, the thermal-conductivity gauge was used, calibrated with the aid of another apparatus against a precise McLeod gauge. Partial pressures in gas mixtures were determined mass spectrometrically. Both instruments covered the range from 10^{-4} to 10 Torr.

In the thermal-conductivity gauge, a tungsten filament of diameter and total length of 3×10^{-3} and 13 cm, respectively, was employed; the V-shaped filament was spanned by means of a spring in a cylindrical cell (of diameter 3.5 cm) with the walls cooled at 0°C. Prior to calibration, the measuring filament had been passivated by glowing in air (pressure of 10 Torr) so that its calibration did not change with time. The gauge was operated under conditions of the constant filament temperature of 100°C, *i.e.* of constant resistance (42 Ω). This was achieved by manual balancing a d.c. bridge circuit, the filament being connected as one arm of the bridge. The balance was maintained by adjusting the power input of the bridge. The gauge reading was taken from a calibration curve which represented the pressure dependence of the voltage on the gauge measuring cell (measured by a compensator). The gauge was calibrated for H_2 , D_2 , CO, cyclopropane, and propylene. The precision of calibration was within $\pm 2\%$ in the region of 10^{-3} Torr.

Analysis of Gas Mixtures

Partial pressures of gases were determined by analyses with use of the mass spectrometer MCH 1302 (SSSR) having the resolution power of 80, the mass range of up to 130 m. u., and the electron energy adjustable within 25–150 eV. The gas mixtures were introduced into the ion source by means of a tube from the apparatus (120 cm, diameter of 0.35 cm) and passed as a molecular flow

through a pinhole in an aluminum diaphragm. As was determined by an approximate calculation, the diffusion effect of the order of magnitude of several minutes was involved with such a tube and a pressure of approximately 1 Torr. This fact was necessary to be kept in view with the kinetic measurements; other arrangement, however, was not possible, owing to the mass spectrometer construction. The molecular regime of the flow was chosen with respect to the kind of the experiments made, *i.e.* mainly to the chemisorption measurements (pressure range of 10^{-4} — 10^{-1} Torr). This type of inlet is connected with pumping off the sample from the apparatus, which is of different significance for different gases. For that reason, the flow was carried out semi-continually, *i.e.* kinetic dependences were followed in parts during shorter time intervals lasting approximately 15 min; between the individual intervals the spectrometer inlet was closed. The experiments were not accomplished all with one rate of flow into the ion source; in case that the orifice with the highest conductivity was used, the rate of pumping off for hydrogen amounted to 19% of the actual amount per one hour. If necessary, some corrections for the losses due to the pumping off were made. The time of flow of 5–10 min, however, was usually needed in view of the source conditioning after the gas introduction.

The mass spectrometer sensitivity was calibrated for carbon monoxide, hydrogen, and cyclopropane through the same passage as used for the introduction of the mixtures to be analyzed. The calibration curves were measured over the whole range of followed pressures, since the sensitivity given by the recorded height of a selected peak in the spectrum was not strictly constant within the whole range under investigation. In the case of other gases in the reaction mixtures, for which the direct calibration from the apparatus was not possible (methane, ethane, propane *etc.*), the determination of partial pressures was based on mathematical conversion of the values for cyclopropane by means of relative sensitivities. The relative sensitivities for these gases with respect to cyclopropane were established using the own inlet system of the mass spectrometer; as far as it was possible to check it up, (*e.g.* with CO), they were the same as the relative sensitivities obtained by direct flow from the apparatus. Absolute sensitivities measured from the apparatus were always approximately by 6% lower, obviously due to the fact that a flow in the inlet tube was involved.

The main problem of determining partial pressures consisted in the attainment and control of the constant values of the ion source sensitivities for individual gases. The sensitivities to hydrocarbons remained usually constant approximately within $\pm 3\%$, but running checks were necessary. Considerable changes in the fragmentation patterns were relatively rare, provided that exact focussing of the source was always kept. The sensitivities to CO and H₂ varied much more distinctly and it was necessary to check and recalibrate them frequently.

In some experiments, mixtures containing certain quantities of hydrocarbons having more than three carbons were obtained. It was not possible and owing to their quantity even not useful to obtain own fragmentation patterns and the values of sensitivity for all of them. In these cases, tabulated spectra and relative sensitivities were employed. The data were taken from a catalogue, where the spectra of the C₁–C₃ hydrocarbons were obtained by means of the same mass spectrometer as the spectra of higher hydrocarbons⁹. Since the tabulated data for the C₁–C₃ hydrocarbons were in good accordance with those achieved with the use of our instrument, the relative error of the calculated concentrations of higher hydrocarbons should not exceed $\pm 10\%$.

Experimental Procedures

a) *Chemisorption of cyclopropane and/or its subsequent selfhydrogenation.* In these experiments, the cyclopropane doses were measured by the thermal-conductivity gauge. If selfhydrogenation took place, then starting from a certain dose, a residual pressure of products was detected and a slow process of cyclopropane consumption was observed. The kinetics of chemisorption and

disproportionation were sometimes studied by mass analysis¹⁰. However, as a consequence of the pumping off, the frequent analyses tended to impair the quantitative aspect of the chemisorption process, to which the experiments made up to now were rather orientated. Therefore the detection of the time change in the composition of the gas phase by means of the thermal-conductivity gauge was employed, without any claim to the exact quantitative meaning of this reading. The attainment of the limiting state was checked by the mass spectrometric analysis in final stages only of the kinetics of the given dose. The concept of the limiting state is (especially for iron) somewhat arbitrary and depends on the accepted convention when defining the "zero" rate of the adsorption of hydrocarbon under a given pressure. In the present paper, this rate has been defined as a state in which for a period of approximately 1 hour no greater changes in the composition of the gas phase, than within several percents, took place. In this manner, the indicated values of the cyclopropane pressure established in individual doses should be understood, as well.

In most cases, the portion of products that was contained in the dosing volume (*i.e.* in the volume in which the thermal-conductivity gauge and the inlet tube were included) had been pumped off, before further dose of cyclopropane was admitted to the film. Thus, needless analyses of the introduced dose could be avoided. Total pumped amounts of individual gases were summed up and added to the amounts produced in the subsequent portion. If no secondary reactions of products occur, this procedure is equivalent to their accumulation over the film.

The extrapolated coverage at which the formation of products was first observable is further denoted by q^* . Since it was in most cases relatively sharply defined, it was also used as a relative measure of the surface area¹. The total coverage of the surface with residues, achieved in the last dose, is denoted by q_{tot} and evaluated by the number of C atoms on the surface. For its definition, the same is valid as has been said about the limiting state in a dose. The obtained surface layers were further characterized by the relative hydrogen content, *i.e.* by the H/C ratio calculated according to Roberts¹¹ from the known quantities of reactants and products. If the disproportionation was connected with a cracking process, the extent of cracking was given as the percentage content of the C atoms in methane and ethane, referred to the total amount of C atoms in the products.

b) *Displacement of chemisorbed particles by carbon monoxide.* The carbon monoxide doses measured by the thermal-conductivity gauge were admitted onto the films which were covered with chemisorbed hydrocarbon residues to a various extent. Desorbed gases were analyzed by the mass spectrometer, and if the predominating hydrogen was concerned, its quantity was checked by measurement with the thermal-conductivity gauge under simultaneous freezing out the hydrocarbons (provided that methane was absent). This check was also possible in the presence of CO (ref.¹²).

c) *Hydrogenation of the adsorbed phase.* Further possibility to obtain data on the adsorbed particles consists in their conversion to the gas phase by reaction with hydrogen. Hydrogenation was carried out either stepwise by several hydrogen doses or by using only one larger dose. The first procedure led to hydrogenation with a gradually decreasing rate in later stages, and for further course of hydrogenation, doses of increasing hydrogen pressure were necessary¹⁰.

The second procedure was employed to find the total extent of hydrogenation of the layer. Hydrogen was then added in a single dose having the pressure of 0.5 Torr and left in contact with the film as long as the hydrogenation of the surface layer could be detected. The detection was based either on the film resistance change or, in the initial stages of hydrogenation, on the decrease of hydrogen pressure, as measured by the thermal-conductivity gauge. Sometimes the composition of products was monitored by analysis (see Results), for the most part, however, the analysis was carried out at the end of the hydrogenation only. For the extent of hydrogenation

and the limiting states of kinetics, the same definitions as in procedure *a* are valid. During the whole hydrogenation process the products were collected at the temperature of -195°C so that no secondary reactions of the products after their desorption from the surface were possible.

d) *Exchange of hydrogen of the adsorbed layer by deuterium.* These experiments allowed to characterize qualitatively the reactivity of hydrogen in adsorbed layers. They were primarily directed to the metals where no complete hydrogenation of the layer was possible (nickel, molybdenum, iron). When added to a film with an examined preadsorbed layer, deuterium was partly adsorbed, while light hydrogen appeared in the residual gas. From the quantity of the adsorbed deuterium and from both the composition and pressure of the gaseous isotopic mixture, the number of H atoms which were originally present in the adsorbed layer and took part in the process of exchange could be calculated. This hydrogen fraction, which is exchangeable with deuterium, is given by

$$X = [n_{\text{H}}(\text{g}) + Q n(\text{a}) - m_{\text{H}}]/(1 - Q) \quad (1)$$

Here, Q is the ratio of concentrations of H and D atoms in the gas phase, $n_{\text{H}}(\text{g})$ being the number of the H atoms. $n(\text{a})$ is the number of atoms which were adsorbed upon addition of deuterium, m_{H} is the amount of the hydrogen atoms contained in the deuterium dose (isotopic dilution). This expression does not take into account the isotopic effect on adsorption and exchange. Consequently, the value X is somewhat greater than the real exchangeable fraction.

e) *Catalytic reaction of cyclopropane with hydrogen.* As has been already mentioned above, the apparatus was not constructed particularly for kinetic measurements. The conditions of mixing in the inlet system as well as in the apparatus itself were not favourable for the study of fast reactions by mass spectrometry. Nevertheless, with relatively slow reactions or in an effort to get at least qualitative information, the kinetics were studied. The hydrogenation of cyclopropane was carried out on the surfaces obtained in the experiments of the *a* or *c* types in roughly equimolar mixtures with hydrogen, under a total pressure of 0.6–1.0 Torr usually. The reaction mixtures were analyzed; the hydrogen pressure was not read off.

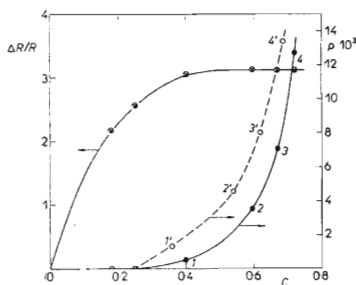


FIG. 3

Chemisorption of Cyclopropane on Iron Film at 0°C

C Adsorption of cyclopropane (μmol); ○ pressure (Torr) established after a rapid adsorption from the corresponding dose (1', 2', 3', 4'); ● pressure (Torr) after additional slow adsorption (1, 2, 3, 4); ⊙ relative increase of the film resistance (%).

RESULTS

Chemisorption of Cyclopropane at 0°C

The admission of the cyclopropane doses onto clean iron surfaces at 0°C led initially to an immediate adsorption that, for higher coverages, was followed by a very slow process in which unreacted cyclopropane was left over the film. Other hydrocarbons or hydrogen were not detected in the gas phase. In Fig. 3, both the quantities attained by the rapid adsorption from the doses and those obtained by the additional slow sorption always after c. 90 min under the corresponding cyclopropane pressure are illustrated. It was found from the condensation of the gaseous phase and measurement of the condensate amounts that all cyclopropane was bound irreversibly to the surface, *i.e.* it was not desorbed.

The chemisorption of cyclopropane was accompanied by an increase of the film resistance, this increase being essentially finished at the coverage where the slow adsorption of cyclopropane occurred and further chemisorption did not change this resistance.

Chemisorption on the Surface Covered with Hydrogen at 0°C

In Fig. 4, changes in the film resistance due to the admission of cyclopropane onto an iron film covered by irreversible chemisorption of hydrogen are plotted. The adsorption of cyclopropane led to a small decrease in the film resistance. A repeated adsorption showed that the decrease in question was reversible. Only a very small adsorbed amount was found, which was likewise reversible within experimental error. The preadsorbed hydrogen was consequently able to protect the surface against the

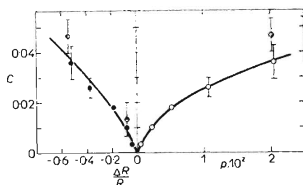


FIG. 4

Adsorption of Cyclopropane on the Iron Film Surface Covered by Irreversible Chemisorption of Hydrogen at 0°C

C Adsorbed amount (μmol); p pressure (Torr); $\Delta R/R$ relative decrease of the film resistance ($^0/_{00}$). In addition, values obtained after pumping off the gas phase (\bullet) and upon repeated adsorption (\odot , \ominus) are plotted.

strong chemisorption of cyclopropane, and essentially allowed only a slight reversible adsorption of the latter, which showed an opposite effect during the resistance change.

Chemisorption of Carbon Monoxide on the Cyclopropane Layer

The surface covered with cyclopropane at 0°C was able further to chemisorb a large amount of carbon monoxide, hydrogen being desorbed as the only product. The

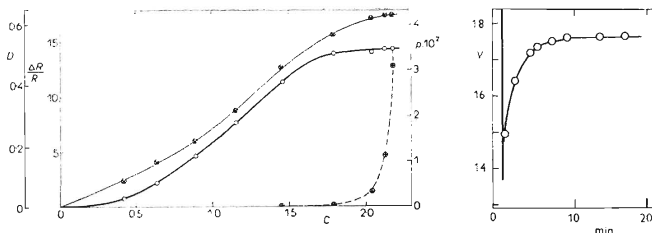


FIG. 5

a Chemisorption of Carbon Monoxide on the Iron Film Surface Covered with Cyclopropane at 0°C

C Adsorbed amount of CO (μmol); C displaced hydrogen amount D (μmol); \otimes relative increase of the film resistance $\Delta R/R(\%)$; \bullet the CO pressure in Torr (p). Preadsorption of cyclopropane 0.37 μmol .

b Time change in the thermal-conductivity gauge reading (arbitrary units) on introduction of a single CO dose.

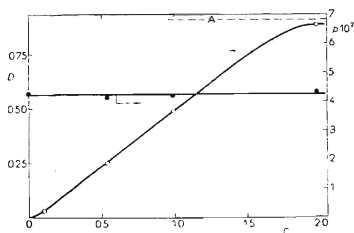


FIG. 6

Displacement of Preadsorbed Hydrogen from the Iron Film During Chemisorption of CO in the Presence of Gaseous Cyclopropane at 0°C

C Adsorption of CO (μmol); D desorbed hydrogen amount (μmol) (\bullet); p cyclopropane pressure in Torr (\bullet). Preadsorbed hydrogen amount is denoted by A .

dependence of the amount of displaced hydrogen on the quantity of chemisorbed CO (Fig. 5) has an S-shaped character, *i.e.* hydrogen was desorbed predominantly at medium coverages with carbon monoxide. The reading of the thermal-conductivity gauge followed during adsorption of one dose (curve in Fig. 5b) suggested a rapid initial chemisorption of CO with the subsequent slow desorption of hydrogen. This behaviour is analogous to the desorption of hydrogen alone due to displacement by CO from iron films¹².

Complete coverage with carbon monoxide brought about a ratio of chemisorbed CO to preadsorbed cyclopropane, amounting to 5.2 ± 0.2 (for 4 films), and the residue left on the surface after the displacement of hydrogen reached a ratio $H/C = 1$, *i.e.* a half of the hydrogen amount originally present in the adsorbed molecules was displaced.

Interaction of Cyclopropane with Hydrogen Labilized during the Displacement

It was shown¹² that on iron carbon monoxide converts hydrogen to a weakly adsorbed form from which desorption at 0°C occurs. A question has arisen whether this labilised hydrogen does not show some extraordinary reactivity, *e.g.*, towards cyclopropane. For that reason, cyclopropane was admitted to the iron surface covered by irreversible preadsorption of hydrogen at 0°C, and this hydrogen was gradually displaced by introducing carbon monoxide doses, whereby certain transient concentration of the weakly bound form was always produced. However, the result in Fig. 6

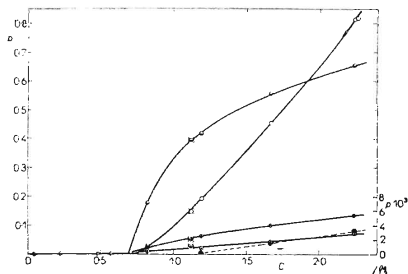


FIG. 7

Chemisorption and Disproportionation of Cyclopropane on Iron Film at 50°C.

C Consumption of cyclopropane (μmol); P amounts of products (μmol); \bullet hydrogen, \circ propane, \odot ethane, \oplus methane; \bullet established cyclopropane pressure (Torr). Framed points correspond to an incomplete reaction of the dose.

shows that no reaction with cyclopropane occurred; its pressure remained constant during the whole displacement.

The displacement of hydrogen was complete; in its course, the ratio of the H_2 desorption to the CO adsorption was roughly constant and equal to 0.5. The total ratio of the monolayers of CO and H_2 amounted to 1.8.

Chemisorption and Disproportionation of Cyclopropane

At 50°C and low coverages, the chemisorption of cyclopropane on an iron film took place immediately (doses 1 and 2, Fig. 7). With the increase of coverage, a slow sorption first appeared, during which no products of interaction were formed. After attaining certain occupancy q^* of the surface, the mass spectrometric analysis established partly selfhydrogenation and cracking of cyclopropane, partly considerable desorption of hydrogen from the layer hitherto produced. The iron surface being fully covered by chemisorption of cyclopropane at 0°C, only a slight desorption of hydrogen occurred by heating up to 50°C. Just starting from this coverage, a further chemisorption of cyclopropane accompanied by disproportionation could then proceed at 50°C, which means that exactly the q^* layer was involved (Fig. 8). The course of propane production was apparently more complicated than in cases studied so far¹. In addition, the presence of hydrogen gas, which probably underwent slow secondary reactions (with gaseous cyclopropane, adsorbed layer), had an influence on the reproducibility of the distribution of products. The cracking led to predominant production of methane and the proportion of cracking decreased with the

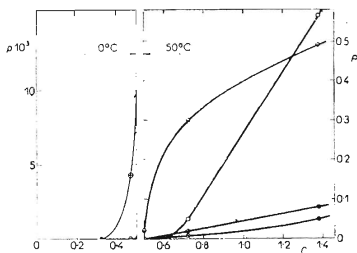


FIG. 8

Chemisorption of Cyclopropane on Iron Film at 0°C (Left) and the Subsequent Disproportionation of Cyclopropane on the Resultant Layer after Heating to 50°C (Right)

C Consumption of Cyclopropane (μmol); ● cyclopropane pressure (Torr) (p); P products (μmol): ○ hydrogen, ○ propane, ⊙ ethane, ⊕ methane.

gradual saturation of the surface. Desorption of hydrogen limited in a similar manner.

Higher coverages of the surface resulted in a very slow adsorption, this having an unfavourable effect on the determination of the q_{tot} value. For the sequence film (9) and film (10), the values $q_{\text{tot}} = 1.93$ and $2.14 q^*$, respectively, were attained. At this stage, the layer adsorbed on the surface had the H/C ratio of 1.04 and 1.17, respectively, while cracking was represented by the amount of 10.2 and 7.9% of the C atoms of the total gaseous product (the same sequence of the films).

Hydrogenation of Chemisorbed Cyclopropane Layer

At 0°C, the chemisorbed layer was not hydrogenated; merely a further adsorption of hydrogen occurred. A portion of chemisorbed residues in the q_{tot} layer (film (9)) could be hydrogenated at 50°C. The hydrogenation was accomplished using one dose of hydrogen under a pressure of $3.2 \cdot 10^{-1}$ Torr, and the attainment of the limiting state was monitored by mass analysis. In Fig. 9, the time dependence of the spectrum of products (ion currents on significant masses) during hydrogenation has been plotted. Calculation of concentrations and distribution of products (Fig. 10) has been made for the final mass spectrum only. Nevertheless, it can be seen from

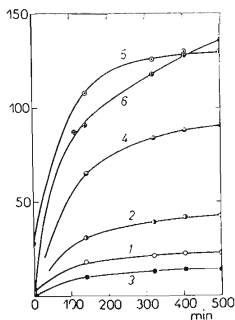


FIG. 9

Time Dependence of Ion Currents on Selected Masses in Spectrum of the Product, Achieved during Hydrogenation of the q_{tot} Cyclopropane Layer on Iron at 50°C

Mass: 1 44, 2 43, 3 30, 4 29, 5 28, 6 16.

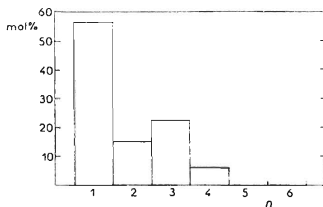


FIG. 10

Product Distribution Obtained by Hydrogenation of the q_{tot} Layer of Cyclopropane on Iron at 50°C, According to the Number of C-Atoms in Molecules

Fig. 9, that, *e.g.* methane (the corresponding mass of 16), was released even after the virtually finished desorption of the other components, and the polymeric products (the currents ratio of masses 44 and 43 is always < 1) were present from the very beginning of the hydrogenation. The final distribution of products (Fig. 10) neglects some trace amounts of unsaturated hydrocarbons. *n*-Butane and isobutane were involved approximately in the ratio 1 : 1.

The maximum hydrogenation extent was not great even at 50°C: it was possible to remove 18% of C atoms originally present in the q_{101} layer.

Exchange of Hydrogen in the q_{101} Layer by Deuterium

After the gaseous products had been pumped off from the film (10) covered to the extent of q_{101} by disproportionation of cyclopropane at 50°C, the exchangeability with deuterium of hydrogen left on the surface was tested. Deuterium was added in one dose (pressure of $6.7 \cdot 10^{-2}$ Torr) and the composition of the isotopic hydrogen mixture was gradually examined at the temperature of -78°, 0°, and 50°C by mass spectrometric analysis. The results are plotted in Fig. 11 as the time dependence of the fraction of exchangeable H atoms, calculated from equation (1). The course of this dependence shows that the layer under investigation contained hydrogen atoms that differed mutually in the reactivity towards exchange. At 0°C, a certain amount (about 60%) of H atoms was exchanged distinctly more rapidly than the rest of them in the chemisorbed layer. Nevertheless, at the temperature

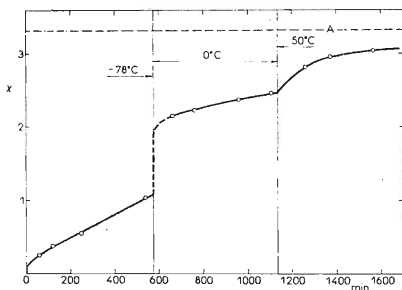


FIG. 11

The Deuterium Exchange of Hydrogen of the Cyclopropane q_{101} Layer Produced at 50°C on Iron
 X Hydrogen amount (μgatom) exchanged within a given time period; A hydrogen amount initially present in the layer (μgatom).

at which selfhydrogenation takes place, all the hydrogen present could be exchanged after a sufficiently long time.

Reaction in the Mixture of Cyclopropane with Hydrogen

At 0°C, no reaction of the gaseous mixture of cyclopropane with hydrogen could be observed, with both the cyclopropane and hydrogen preadsorption. The reaction could be followed at 50°C, for example on the surface obtained by hydrogenation of the q_{tot} layer of cyclopropane after pumping off the mixture of hydrogen with hydrocarbons. The time dependence of partial pressures, obtained by analysis during the course of the reaction, is presented in Fig. 12. It shows that the hydrogenation

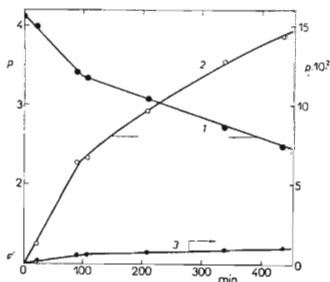


FIG. 12

Time Course of the Reaction in the Mixture of Cyclopropane with Hydrogen on Iron Film at 50°C

p Pressure in Torr of: 1 cyclopropane, 2 propane; 3 approximately equal pressures of methane and ethane. The initial pressure of hydrogen was $3.9 \cdot 10^{-1}$ Torr.

of cyclopropane to propane was accompanied by hydrocracking to methane and ethane; the polymers, however, were not produced. The proportion of hydrocracking amounted to 7% of C atoms of the whole reaction product. No smooth curve fitted the time dependence presented in Fig. 12. This means that, at a relatively low conversion, a sudden decrease of the rate of reaction occurred. A similar behaviour of the kinetic dependence has been observed with the hydrogenation of cyclopropane on other metals¹³ too. We probably encounter here with the effect found earlier in the reactions of acetylenic hydrocarbons¹⁴, of which no sufficient explanation has hitherto been given.

DISCUSSION

As already shown¹, two alternatives of interaction of carbon monoxide with a layer of dissociatively chemisorbed hydrocarbon are generally possible. When being replaced from their adsorption sites, the hydrogen atoms can recombine either mutually or with hydrocarbon residues. The relative feasibility of both processes is dependent on the given metal, particularly on its capability to catalyze recombination of C—H bonds in the surface layer of chemisorbed complexes. The absence of hydrocarbons in the product of displacement by carbon monoxide on iron suggests a low effectiveness of iron in the above recombination, from which we may infer that the H/C ratio obtained with the carbonaceous residues after the hydrogen displacement corresponds even to the composition of originally chemisorbed residues (*i.e.* prior to the desorption). No data at all exist on the extent of dissociation of the C—C bonds in the layer chemisorbed at 0°C. The composition of these residues may then be written in the form $[\text{CH}]_n$ only, where $n = 1-4$ can occur according to the below-discussed results of the hydrogenation of the layer produced at 50°C. Owing to the relatively small extent of coverage and the experimentally found decrease of the cracking portion in the overall product of disproportionation during the increasing coverage (Fig. 7 and 8), n may approach unity.

In order to understand the mechanism of selfhydrogenation, we shall try to consider the results primarily from the viewpoint of the fundamental problem as to whether the saturated products originate in the impact of the cyclopropane molecule from the gas phase against the site occupied by a pair of hydrogen atoms¹⁵⁻¹⁷, or whether a redistribution of hydrogen between the molecules being in the adsorbed form takes place¹⁸⁻²⁰. The displacement by means of CO showed that, even at 0°C, cyclopropane is chemisorbed with some C—H bonds dissociation. If we take into account the overall character of disproportionation at 50°C, then, even if we assume the reaction of the impacting molecule, this idea must be at least modified in that respect that hydrogen is reactive apparently from a certain concentration only of the H atoms on the surface or from a certain total coverage of the surface. This would mean that the presence of a not strongly bound hydrogen is a condition of the selfhydrogenation process. We can then hardly understand, however, why hydrogen is sometimes desorbed during the selfhydrogenation, as found in our case and, for example, also in the system ethylene—chromium¹⁶.

In spite of fact that on the surface, irreversibly covered with chemisorbed hydrogen, a slight reversible adsorption of cyclopropane occurred, the chemisorbed hydrogen neither reacted at 0°C with the impacting cyclopropane molecules, nor was it displaced. Obviously, neither impact of the cyclopropane molecule against a pair of H atoms, nor its presence on the surface in a weakly bound form were sufficient for its hydrogenation. According to this mechanism, the effect of the temperature rise up to 50°C (which leads to selfhydrogenation) would essentially consist in the enhanced activation of adsorbed hydrogen, as has been mentioned above. Since a mere increase

in the reactivity of adsorbed hydrogen by rising the temperature is not possible without any activation and chemisorption of cyclopropane taking place, an attempt was made to prepare labilized hydrogen in the presence of gaseous cyclopropane directly in "nascent state" by using displacement by means of carbon monoxide. Even in this case, no reaction of weakly bound hydrogen with cyclopropane was observed.

In the light of the results discussed up to now, that mechanism of selfhydrogenation seems to be the most probable in which the surface interaction of the adsorbed particles is involved. In addition, dissociation of molecules in the C—C and C—H bonds on chemisorption does not seem to be the difficult step in this mechanism. As will be shown later, some general features of the selfhydrogenation process, *e.g.*, the defined character of the coverage q^* , the presence of slow processes leading to q_{tot} , and the temperature dependence of the extent of coverage, may be simply explained under the assumption that recombination of the C—H bonds in the surface layer, associated ultimately with desorption, plays a decisive role.

In an attempt to elucidate the role of the split-off hydrogen in the cyclopropane layer chemisorbed at 0°C on iron, it was tested whether the selfhydrogenation proceeded in the surface layer, *e.g.*, due to the decomposition of the chemisorbed cyclopropane during the temperature rise from 0°C to 50°C. We find, however, that adsorption at 0°C provides only such a coverage of the surface, which represents approximately the q^* layer for those temperatures at which selfhydrogenation takes place. In other words, if recombination of hydrogen and carbonaceous intermediates does not proceed on the surface — either because of the temperature being too low for this activated step (0°C in our case), or that coverage of the surface is not sufficient for hydrogen to be labilized (coverage $< q^*$ at 50°C), the selfhydrogenation is not possible. At the low temperature, not even further cyclopropane chemisorption takes place, in spite of that the surface saturation is not maximum, some additional free sites persist, *etc.* No removal of hydrogen and its substitution by additional carbonaceous complexes takes namely place at the q^* coverage in the absence of the recombination connected with desorption. Under these conditions, the surface then behaves as effectively covered with respect to cyclopropane.

The data achieved by hydrogenation of the q_{tot} layer clearly show that gradual recombination with the surface hydrogen is not possible for all the adsorbed particles, or does not lead as far as to the desorption of the hydrocarbon. Moreover, a comparison of the product of hydrogenation and that of the catalytic reaction at the same temperature points to non-participation of the surface complexes, formed by association (polymerization) of primary particles, in the catalytic reaction. The reason why the polymers do not react in the presence of cyclopropane is likely of kinetic nature and was discussed elsewhere¹. Here, the conclusion of importance is that the extent of hydrogenation of the layer is generally greater than the portion of chemisorbed residues taking part in the reaction. It may be of use to mention

here the results of the radiotracer experiments of Thomson and coworkers^{21,22} with ethylene on transition metals, where, after the exchange of a part of preadsorbed labelled ethylene during the hydrogenation of gaseous unlabelled ethylene, no further removal of the residues by hydrogen treatment of the layer could be detected. Another fact important for us is the finding of the latter authors that, as far as the participation in the catalytic hydrogenation reaction was concerned, there was no difference between the initial and last portions of ethylene layer consecutively preadsorbed on nickel²³. With reference to the evident dissociative adsorption in the q^* layers, we can say that, likewise, the dissociative chemisorption of a cyclopropane molecule is generally not prohibitive for its further role of an intermediate in the hydrogenation reaction.

In our recent study on the hydrocracking of cyclopropane on nickel² it was possible to distinguish between a specific low-temperature splitting to methane and ethane, and a high-temperature nonspecific process leading to the predominating formation of methane. In the specific process, the ratio of the rates of hydrogenation and hydrocracking was independent of conversion (*i.e.* the partial pressures of reactants) and constant over a wide range of temperature (195–500°K). With iron, the temperature dependence of selectivity has not been studied; it is possible, however, to compare the composition of our reaction product (at 323°K) containing methane, ethane, and propane in relative molar ratios 1 : 1 : 13, and the result of Anderson and Avery²⁴, who found (at approximately 440°K) the relative molar proportions 1 : 0.42 : 0.58. It is obvious that if on iron the specific type of cyclopropane splitting takes place, this occurs to a much smaller extent than on nickel; the nonspecific process, however, is detectable even at a considerably lower temperature. The great tendency of iron to a complete degradation of the cyclopropane molecule manifests itself also during disproportionation by formation of an excess of methane when compared with ethane. At the same time, the composition of the products of hydrogenation of the resultant layer suggests that the lower production of ethane is not likely due to a preferential retention of two-carbon complexes on the surface during disproportionation. Similarly, the nonlimiting excessive formation of methane during hydrogenation of the q_{tot} layer at 50°C may be explained as a slow hydrogenation destruction of strongly attached complexes remained on the surface. However, the considerations about the nature of these residues (80%) would be speculative at present.

The author remains deeply indebted to the late Professor R. Brdička for his having made possible this work at the Institute of Physical Chemistry. Further thanks are due to Dr V. Ponec for his support during the investigations and Dr Z. Knor for valuable discussions.

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Translated by J. Hejduk.