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Chemisorption and Hydrogenation of Cyclopropane on Nickel

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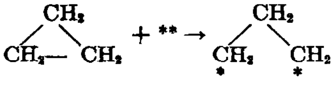
Chemisorption of cyclopropane was investigated by measuring the extent of chemisorption on nickel film of known sufrace area, measuring the changes of electrical resistance of the film during chemisorption, and performing mass spectrometric analysis of the gas phase. It was found that during interaction of cyclopropane with nickel the C–H and C–C bonds are split.

Some measurements of cyclopropane hydrogenation on nickel at 273°K and under static conditions were made. Cyclopropane reacts with hydrogen in a rather complicated way as is shown by the presence of ethane in the reaction mixture. After pumping off the reaction mixture from the apparatus and admitting a starting mixture, hydrogenation on the same film proceeds with the same velocity. By poisoning nickel with oxygen before and after the first reaction, it was shown that only a small part of the surface and/or of the adsorbed layer participates in the reaction under given conditions.

The catalytic hydrogenation of cyclopropane on metals was described at the beginning of this century (*1*). This reaction was investigated later in greater detail by Bond and co-workers (*2–5*) who obtained very valuable results, particularly with the use of deuterium (*4, 5*). It appears that the hydrogenation of cyclopropane involving isomerization of cyclopropane to propylene is very improbable. This is also in good agreement with the fact that isomerization of cyclopropane proceeds more readily on catalysts of acido-basic character, whereas on metal catalysts the reaction takes place only at higher temperatures (*4, 6, 7*). This statement was also confirmed by recently published results on the influence of mercury poisoning (*8*).

On the basis of kinetics the authors of the mentioned papers arrived at the additional conclusion that cyclopropane is adsorbed either with an opening of the ring bond (*2–5*)



or with the participation of delocalized π electrons of cyclopropane (*3*). The usual interpretation of the kinetic data induced these authors (*2–5*) to believe that cyclopropane is less firmly bound to metal surfaces than hydrogen.* If this conclusion is correct, the hydrogenation of cyclopropane should proceed without the complications which accompany, e.g., the hydrogenation of ethylene (*9–11*).

EXPERIMENTAL

The measurements of the extent of chemisorption of gases and of the physical adsorption of krypton and the measurements of the course of catalytic reactions were carried out in a static apparatus, described earlier (*12*). On this all-glass apparatus no greased cocks or joints were used; the adsorption (reaction) vessel was sealed to the apparatus. The apparatus operated with mercury cutoffs. The adsorption (reaction) vessel and the ionization

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* Note added in proof: This view was stated again in a recent paper: NEWHAM, J., *Chem. rev.* 63, 123 (1963).

gauge of the Bayard-Alpert type were protected against mercury vapor by means of cold traps. The apparatus was evacuated by two mercury diffusion pumps in cascade, backed by a mechanical pump and two bulbs filled with active charcoal. During evacuation all apparatus was heated by heating tapes. With traps at 78°K, it was possible to obtain a vacuum of the order 10^{-8}–10^{-9} mm Hg after 4–5 days of evacuation. With traps at 195°K the vacuum obtained during the same time interval was only 10^{-7} mm Hg. The nickel wire used for evaporation of the film contained no other metals in amount higher than that contained in a spectroscopical standard. However, it contained about 0.2% of MgO and SiO_2. The pressure changes during sorption and catalytic reaction were measured by two McLeod gauges (constants for the quadratic scale were: 1.3×10^{-6} and 0.85×10^{-4} mm^{-1}).

The thermomolecular effect (*12*) in tubes 14 mm in diameter as used in our apparatus may be neglected at 195°K at pressures of about 10^{-2} mm Hg in the given apparatus, since the constant Φ_g of the Liang equation (*13*) modified by Bennett and Tompkins (*14*) has a value of 6–7 (*15*).

The mass spectrometer was employed for the analysis of the products of catalytic reaction, of the products of chemisorption of cyclopropane, and for the purity control of gases used. The sampling tube for analysis was always immersed in liquid nitrogen, the condensable gases were frozen out in it, and after sealing off, the tube was transferred to the mass spectrometer. The mass spectrometer used was of the Nier type (*17*). The samples for analysis contained 0.5–5 μmoles of the gas.

The cyclopropane was a product of I.C.I. (G.B.) for medical purposes. The purification of cyclopropane was carried out in a special apparatus. The gas was first submitted to distillation at temperatures of 195°K and 78°K and then was distilled into glass reservoirs. A part of each reservoir was cooled down to 78°K, the gas phase was pumped off and this procedure was repeated twice. Then the reservoir, a part of which was immersed in liquid nitrogen, was sealed off from the distillation apparatus and connected to the measuring apparatus. Prior to each experiment a small sample of cyclopropane (2–5 1mm Hg) was repurified by pumping off gases noncondensable at 78°K. This was continued until the pressure over the solid cyclopropane (kept at 78°K) was $\leqslant 10^{-6}$ mm Hg. Cyclopropane prepared in this way contained less than 0.1% nitrogen, 0.2% propane, 0.5% methane, and 1% ethylene.

The changes of electrical resistance of the film caused by chemisorption and surface reaction were measured in an adsorption vessel with platinum contacts (*16*). The resistance was measured by direct current on a Wheatstone bridge.

For comparison, the measurements of the catalytic activity were also carried out on nickel powder which was prepared by decomposition of nickel oxalate *in vacuo*. During decomposition the temperature gradually rose from 520 to 573°K. After decomposition was complete the sample was further evacuated for 5–7 hr at a maximum temperature of 623°K. The specific area of the nickel powder obtained by this procedure was 8–10 m^2/g, and so was practically the same as that of nickel films used in this work, i.e., ca. 10 m^2/g.

RESULTS

Sorption of Cyclopropane

If a single fairly large sample of cyclopropane is admitted to the film at 273°K, about 80% of the "total sorbed amount" is taken up from the gas phase during the first minute. The sorption of the remaining part proceeds more slowly. After about one hour, the slow pressure drop ceases (the final value of the pressure at the end of the slow process was in the range $2\text{–}5 \times 10^{-2}$ mm Hg). The "total sorbed amount" corresponds to this state ($1\text{–}6 \times 10^{-6}$ moles for various films). In this stage the samples were taken for the mass spectrometric analysis. Each sample contained all gases condensable at 78°K which were present in the gas phase at the end of the slow process and also those gases which desorbed from the film into the sampling tube when the tube was immersed in the liquid nitrogen. The entire content of gases noncondensable at 78°K (e.g. N_2, CH_4, H_2, CO) was always less than 1% of the total sorbed amount. The content of hydrocarbons higher than C_3 in the condensed fraction was less than 1%; the content of both ethane and propane was 5–15% of the total sorbed amount. The total amount of ethane and propane corresponded to about 50% of the entire quantity of gas subjected to the analysis and was much higher than the possible error of analysis. However, the samples for analysis were always taken after the same period—1 hr—of contact with the film. Since the surface areas of films were different, the total yield of self-hydrogenation naturally varied—it was found that the entire content of self-hydrogenation products increased with increasing surface area of the film. This was the probable reason for the variations in analyses.

If cyclopropane is added successively in small doses [this method was used, e.g., in refs. (*10, 11*)], then at 273°K 80–85% of the total sorbed amount is sorbed without residual pressure (Fig. 1—part of the curve up to the point A). Between A and B the number of molecules which disappeared from the gas phase amounted to 50% of the number of added cyclopropane molecules. The behavior of cyclopropane is in this respect very similar to that of ethylene (*10, 11*). After admission of a dose of cyclopropane corresponding to point B or of a larger dose, no further uptake of molecules from the gas phase is observed at 273°K.

When the temperature is increased from 200° to 300°K the amount of sorbed gas (at the end of the slow process and at pressures of about 2×10^{-2} mm Hg) rises in the course of the first sorption (Fig. 2, lower branch of isobars). Since the gas phase contains ethane and propane, no quantitative conclusions can be drawn from these data.

After completed sorption at 273°K, the gas phase was frozen out at 78°K; the pressure of noncondensable gases was 10^{-5}–10^{-4} mm Hg. The amount of desorbed gases was determined by evaporating the condensed gases in a separate part of the apparatus. It corresponded to 2–5% of the original sorbed amount. Admission of a fresh dose of cyclopropane to the same film

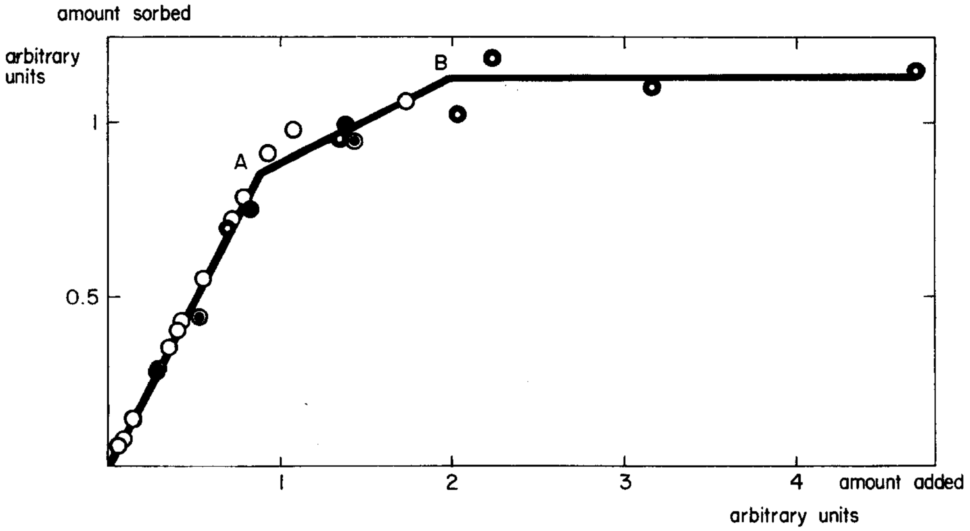

FIG. 1. Amount of cyclopropane admitted to film in comparison with amount of gas which disappeared from the gaseous phase during the particular sorption process at 273°K. Amounts of gas are expressed in arbitrary units. Different symbols represent results obtained from individual experiments.

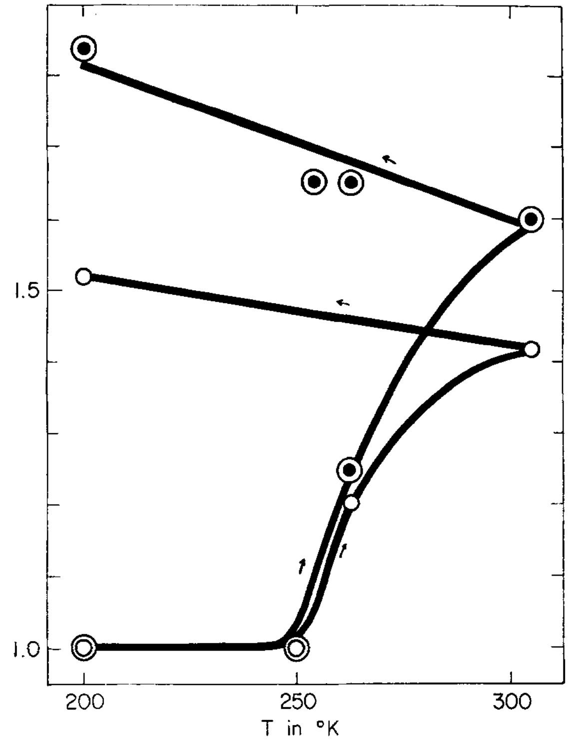

FIG. 2. Variation of the relative sorption of gas from the gaseous phase during cyclopropane sorption with temperature at pressures of about 2×10^{-2} mm Hg. Extent of sorption at 200°K represents $\epsilon = 1$ in units used here. Arrows indicate the increase or decrease of temperature. Individual curves correspond to measurements with two films.

led to a new sorption in an amount of 4–15% of the original sorption. This means that the amount sorbed in the second sorption is two to three times the quantity desorbed. After the second sorption, the gas phase again contained propane and ethane, the total amount of both being 30–50% of the amount adsorbed in the second sorption.

Nickel films on which chemisorption of cyclopropane was investigated were also subjected to measurements of the adsorption of krypton (*20*). It was found that the extent of cyclopropane sorption at 200°K corresponded to an area of about 42 Å^2 per one molecule disappearing from the gas phase at 273°K; the area of the "adsorption site" so defined is 34 Å^2.* The last figure corresponds to approximately four sites for hydrogen atoms at 78°K and 273°K (*18, 19*).

Cyclopropane chemisorption at 273°K causes an increase of the resistance of the clean nickel film, like that of other firmly chemisorbed gases (*21*) (Fig. 3). When hydrogen is admitted at 273°K to the film covered with products of cyclopropane chemisorption the resistance of the film decreases. When the gas phase is pumped off after this interaction the resistance then remains constant or increases little (e.g., 0.5‰ after the 5.5‰ drop caused by interaction with hydrogen).

As already reported earlier, irreversibly bound hydrogen causes an increase of the resistance of the clean film. Cyclopropane

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* Owing to the probable fragmentation of cyclopropane molecules during chemisorption no additional conclusions can be made on the basis of these data about the character of adsorbed particles.

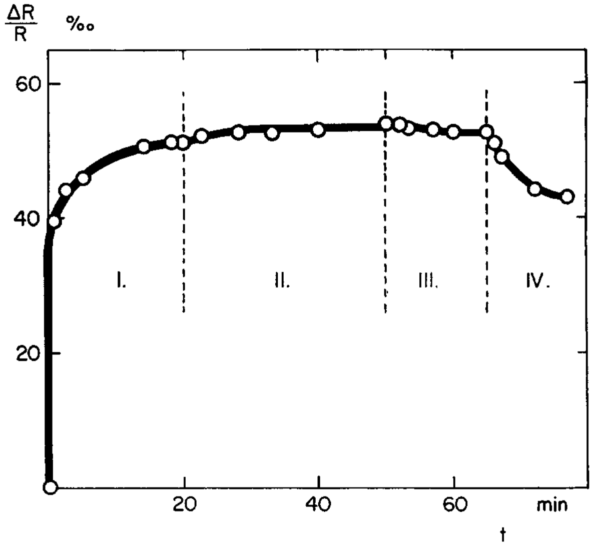

Fig. 3. Change of electric resistance of the film after admitting cyclopropane and hydrogen successively to the film at 273°K. I—first dose of cyclopropane admitted to the clean film, pressure in the gaseous phase at the end of interval I was 1.7×10^{-4} mm Hg. II—second dose of cyclopropane admitted, further sorption took place, pressure at the end of II was 4×10^{-3} mm Hg. III—hydrogen admitted (after evacuation of the gas phase) to the covered surface at 2×10^{-3} mm Hg pressure. IV—hydrogen admitted at the higher pressure, 2 mm Hg.

admitted to a film covered with such a layer of irreversibly bound hydrogen causes a further increase of the resistance of the film (Fig. 4). As the sorption of cyclopropane changes the resistance of the film more strongly than the sorption of hydrogen, it seems that the increase of resistance here is not caused merely by the hydrogen, split from cyclopropane molecules, but also by the carbon-containing fractions of cyclopropane molecules.

After completed sorption of cyclopropane at 273°K and evacuation of the gas phase (maintaining the film at 273°K), the sorption of hydrogen on the film was measured at 78°K. The ratio of the total amount of hydrogen sorbed under these conditions to the total amount of cyclopropane sorbed on the clean film amounted to 0.3–0.6. The reaction between hydrogen and the products of cyclopropane chemisorption at 78°K probably proceeds very slowly. It can be supposed that hydrogen is sorbed presumably on free sites of the film. These results show that the surface covered by strong cyclopropane chemisorption still contains places for hydrogen chemisorption. After the chemisorption of hydrogen, the gas phase was again evacuated (with the film at 273°K). The new sorption of hydrogen repeated at 78°K was of the same extent as in the first measurement.

In addition, some measurements were made with propane at 273°K. Propane is sorbed to a considerably lesser degree than cyclopropane. When the sorption of the gas has ceased, each molecule which disappeared from the gas phase covers about 140 Å². Practically no desorption of condensable gases takes place at 273°K ($<2\%$). The amount of noncondensable gases corresponds to about 0.1% of the sorbed amount (pressure of noncondensable gases was ca. 10^{-5} mm Hg). The gas phase contained ethane and propylene in amount corresponding to 4% and 9%, respectively, of the total amount of propane sorbed at 273°K. When a fresh dose of propane is admitted after evacuation at 273°K, an additional 10% of propane is

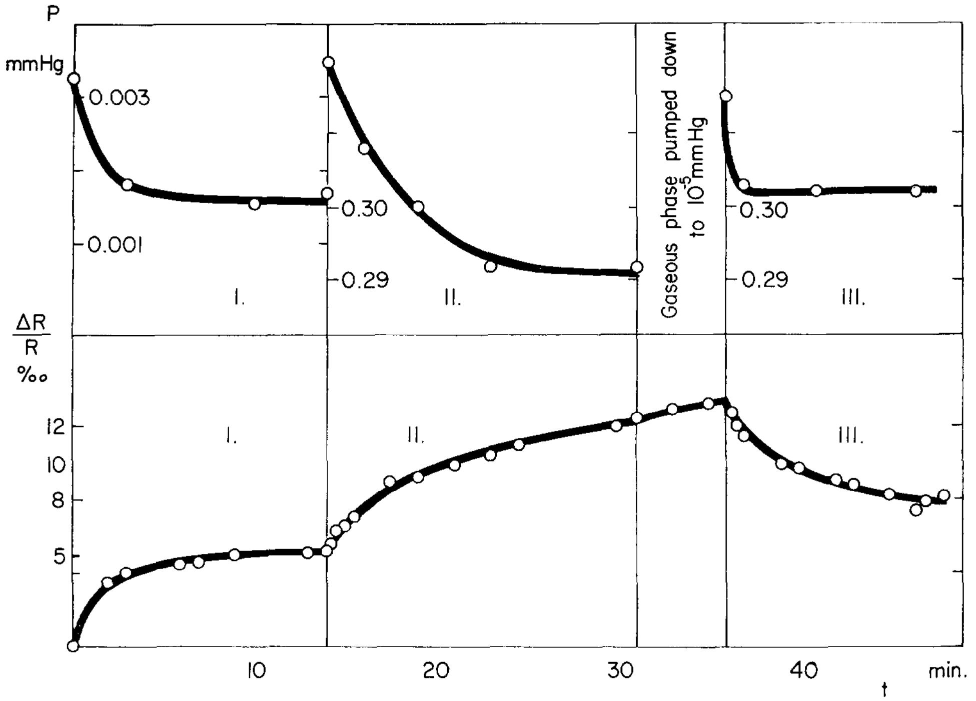

FIG. 4. Changes of electrical resistance of the film (lower part) and simultaneous changes of pressure in the gaseous phase (upper part) during the interaction between hydrogen and cyclopropane at 273°K. Before the beginning of interval I, the surface has been covered by hydrogen irreversibly bound at 273°K. I—cyclopropane added. II—new dose of cyclopropane added. III—hydrogen added after evacuation of the gaseous phase.

sorbed. The desorption from the film was zero, within the limits of error.

Hydrogenation of Cyclopropane at 273°K

This reaction was investigated with an approximately stoichiometric mixture of cyclopropane and hydrogen at a total pressure of 1.2–1.5 mm Hg. The influence of external diffusion was estimated according to Weisz and Prater (*22*) (a tube 2 m in length and 14 mm in diameter was taken for calculations as a model of the apparatus). The influence of internal diffusion was estimated roughly according to Wheeler (*23*). On the basis of these estimates it seems that the influence of internal and external diffusion was probably negligible in our experiments.

During the reaction of cyclopropane with hydrogen the pressure decreases according to the equation

$$\Delta p = a(t + t_0)^m$$

where Δp is the total pressure drop at the time t. The constant m varies between 0.5 and 0.8 and the constant t_0 is very near to zero. Plotting $\Delta p = f(t)$ in bilogarithmic coordinates permits us to determine m and a and thus also the rate of reaction at the end of the first minute:

$$(d\Delta p/at)_{t=1\ \mathrm{min}} = am$$

This reaction rate expressed in number of molecules reacting on 1 cm^2 in one minute will be henceforth denoted by ${}_{s}r_1$.

In the literature there has been some question as to whether the hydrogenation of unsaturated hydrocarbons can be repeated on the same film several times without a decrease of the reaction rate. We have found that the reaction of cyclopropane with hydrogen could be successfully repeated on the same film with the same rate. However, this happens only when the evacuation of the gas mixture between individual runs was carried out so as to prevent possible contamination of the film due to an incidental penetration of impurities from the forevacuum through the last high-vacuum stage back to the film. Such penetration is possible when gas is exhausted from the apparatus at a pressure higher than the working range of pressures of the mercury diffusion pump. To eliminate this shortcoming a vessel filled with well outgassed active charcoal, cooled to 78°K was connected to the forevacuum line. Under such conditions it was possible to repeat the reaction at 273°K several times with the same velocity. The rate on the same film at the same temperature was reproducible within 10% even when a reaction had been carried out at another temperature between runs. However, the reproducibility of the determination of ${}_sr_1$ with different films (this procedure involves the measurement of the surface area of the film) is worse, as can be seen from Fig. 5a.

The mass-spectrometric analysis showed that the reaction yielded besides propane, also ethane in an amount corresponding to about ⅙ of the propane formed. This amount of ethane is much higher than could be ascribed only to the first dissociative chemisorption on the clean surface only. Consequently, ethane is formed in the entire course of the reaction, probably by a slower side reaction. Production of ethane is accompanied by production of methane. However, only gases condensable at 78°K could be detected by the procedure used.

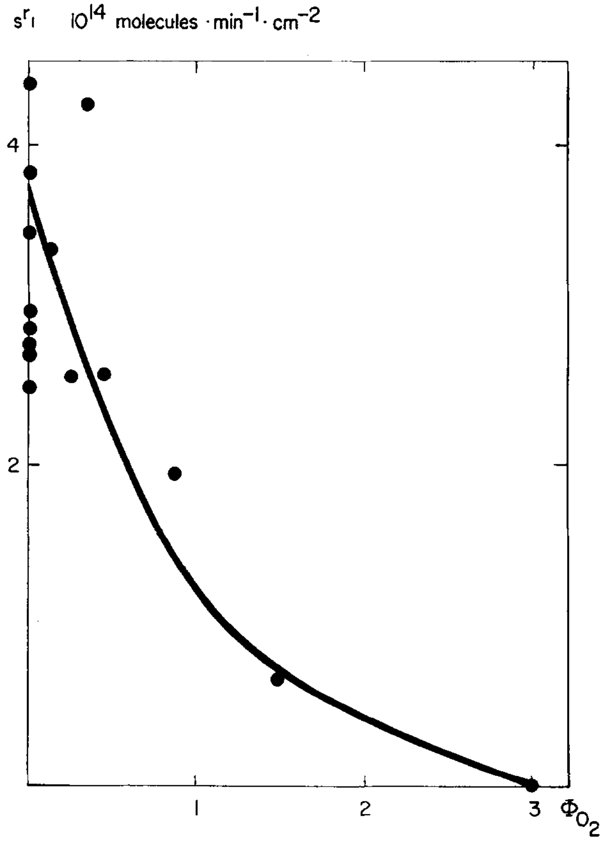

FIG. 5a. Decrease of the rate of hydrogenation of cycdopropane at 273°K (rate expressed in number of molecules reacting in one minute on 1 cm² of nickel surface) with increasing extent of oxygen preadsorption (expressed in arbitrary units).

The preadsorption of cyclopropane and hydrogen is, within the limits of experimental error, without influence upon the course and rate of the following reaction.

The preadsorption of oxygen, before the first reaction on the given film, decreases the rate of the following hydrogenation approximately in the same way and to the same degree (Fig. 5a) as it decreases the extent of hydrogen chemisorption on nickel films at 78°K (Fig. 5b) (*24*).* However, the poisoning of the film by oxygen after the first reaction has been completed is by far more effective. The preadsorption of ca. 3 units Φ_{O_2} prior to the first reaction is necessary for complete suppression of the activity. When the film is poisoned by oxygen after the first catalytic reaction, much smaller amounts of oxygen are sufficient to achieve a similar effect. The sorption of only 0.04 units Φ_{O_2} after the first reaction reduces the reaction rate to about 15% of the original value.

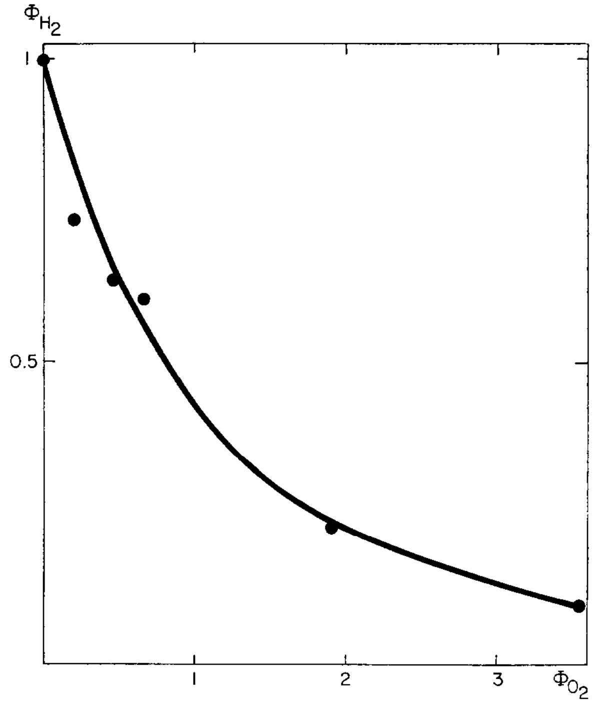

FIG. 5b. Decrease of hydrogen chemisorption at 78°K with increasing oxygen preadsorption (extent of adsorption in arbitrary units).

Films condensed in the presence of an inert gas (krypton pressure ca. 0.15 mm Hg) exhibit a surface approximately twice as large as films condensed *in vacuo,* but their specific activity $_{s}r_{1}$ does not differ essentially from that of less porous films.

After the reaction mixture is pumped off the nickel surface can again sorb the same amount of cyclopropane as can a film covered by irreversibly chemisorbed cyclopropane only.

The activity of vacuum-deposited nickel films was compared in the same apparatus and reaction vessel with the activity of

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* The results are expressed in arbitrary units Φ_{O_2},Φ_{H_2}. These units represent the ratio of the extent of sorption of hydrogen or oxygen under given conditions to the total amount of hydrogen sorbed at 78°K on the clean film of the same surface area. This value can be calculated from the measured surface area and the known size of one hydrogen atom in the adsorbed state [8.3 Å^2 on Ni (*18, 19*)]. In this way the sorbed amounts are expressed in arbitrary hydrogen monolayers.

TABLE 1
Hydrogenation of Cyclopropane on Nickel

${}_sr_1 = a \cdot m$ (10^{14} molecules min^{-1} cm^{-2})	m	Notes
2–4.4	0.5–0.8	Clean films condensed in vacuum
2.8	0.6	Film with preadsorbed hydrogen
2.5–2.7	0.7	Film with preadsorbed cyclopropane
1.2–2.1	0.5–0.7	Clean films condensed in krypton
(0.9–1.0) × 10^{-2}	1.0	Nickel powder from oxalate

nickel powder of approximately (within 20%) the same surface area. It was found that at the same temperature the activity of the film is at least two orders of magnitude higher than the activity of the powder (Table 1). This is in agreement with measurements of hydrogen chemisorption at 78°K, which have shown that the clean part of the surface of nickel powders prepared by decomposition of nickel oxalate *in vacuo* amounts to only a few hundredths of their total surface.

DISCUSSION

The presence of propane in the gas phase after addition of pure cyclopropane to the clean films shows that in some molecules the C–H bonds are split during the interaction of cyclopropane with the nickel surface. The C–C bonds are evidently also split in some molecules since ethane is also present in the gas phase. It can be concluded that the surface of nickel is very probably covered by various fragments of cyclopropane molecules.

Admission of hydrogen to the film covered with cyclopropane results in a drop of electric film resistance. This phenomenon may be explained either by mere chemisorption of hydrogen or as a result of the reaction of hydrogen with the products of cyclopropane chemisorption, or by the influence of both processes. However, if the first case is true one must suppose that the behavior of hydrogen on films covered by products of cyclopropane sorption is quite different from that of hydrogen on a clean film. If there were a reaction (second case) between hydrogen and the chemisorbed phase, the time dependence of pressure, illustrated by Fig. 4 III would show an initial rapid sorption of hydrogen without significant influence upon the electric resistance of the film. This adsorption would be followed by a slow reaction with the chemisorbed particles in the adsorbed layer (slow resistance drop). In the later stage of the surface reaction the pressure does not change further with time, either because one hydrocarbon molecule is set free for each hydrogen molecule disappearing from the gaseous phase, or because the reaction is limited to the adsorbed layer without further participation of the gas phase.

The dissociative character of the chemisorption of hydrocarbons, even of those containing double bonds, is evidently a general phenomenon. This is indicated by the results given in the literature for the adsorption of ethane, ethylene (*10, 11*), benzene (*25*), cyclohexene (*25*), and cyclohexadiene (*25*). The products of chemisorption resulting from one molecule of cyclopropane cover, at 273°K, an area of the nickel film surface equivalent to about 4 sites for hydrogen atoms at 78°K—ca. 43 Å^2. For comparison: One ethylene molecule covers at the same temperature according to Beeck (*26*) four and according to Rideal-Jenkins (*10*) 2.4 hydrogen atom sites at 273°K. In Fig. 6 there is shown an area of 43 Å^2 on the (111) plane of nickel and it is compared with the cyclopropane molecule. Owing to the complicated character of the cyclopropane sorption (self-hydrogenation, splitting of the ring, etc.) the surface is probably not covered by cyclopropane molecules only. So Fig. 6 does not represent the model of the adsorbed layer; it serves only for a very rough estimation of the extent of surface coverage.

The adsorption of hydrocarbons on metal surfaces is probably made easier, if the system of π electron bonds is present in these molecules. As already pointed out, cyclopropane is adsorbed more readily than propane, just as ethylene and acetylene are

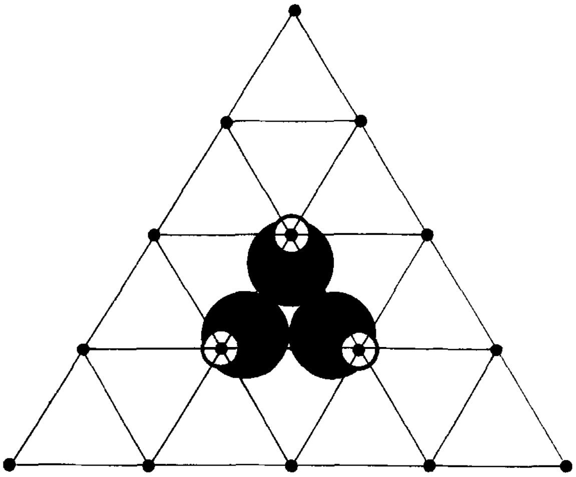

FIG 6. Comparison of the area of 43.2 Å^2 on the (111) plane of nickel with the magnitude of cyclopropane molecule.

adsorbed more readily than ethane. In its chemisorption behavior, cyclopropane resembles ethylene to a considerable degree. This is in agreement with the statement of some authors that in the cyclopropane molecule carbon atoms exhibit sp^2 hybridization and the C–C bond is of partial π character (*27*, *28*).

As indicated by the presence of ethane in the products of chemisorption and hydrogenation, the mechanism of cyclopropane hydrogenation on clean nickel surfaces is a rather complicated process. For this reason, no attempt was made either to interpret the kinetic equation found, or to study the dependence of the initial reaction rates upon partial pressures. The kinetic relation was only used for easier determination of the rate at the end of the first minute of the reaction.

A considerably smaller amount of oxygen is required for the practically complete suppression of the catalytic activity of a film which was already in contact with cyclopropane, than that of a clean film. This is evidently due to the fact that the fast catalytic reaction proceeds mainly on the small number of active sites not covered by firmly bound products of cyclopropane chemisorption.

Numerous authors report that the hydrogenation of ethylene repeated on the same film, without special treatment of the film (reduction), always proceeds with a lower rate (*10*, *11*, *29*, *30*). In our case, however, it was possible to repeat the hydrogenation of cyclopropane several times on the same film without decrease of its activity. A mere exhaustion of the gaseous phase at 310°K was sufficient to regain the original catalytic activity. Moreover, in cyclopropane hydrogenation a higher specific activity of films prepared by condensation in an inert gas (*31*) was not observed. Preadsorption of cyclopropane and hydrogen also never changed the rate of the subsequent reaction.

Vacuum-deposited films have a much higher activity than powder catalysts described in the literature as highly active (*32*). These powders also exhibit a considerably lower adsorption of hydrogen at 78°K. This leads to the conclusion that the lower activity of powders could be explained by the different cleanliness of the surfaces of both types of nickel catalysts.

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