

# SELFHYDROGENATION OF UNSATURATED HYDROCARBONS ON TRANSITION METALS PARTIALLY COVERED WITH PREADSORBED OXYGEN

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

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The effect of preadsorbed oxygen on the mechanism of cyclopropane and propylene interaction with the surface of platinum and nickel was studied. Oxygen influenced both the course of self-hydrogenation and the way of oxidative splitting of the carbon skeleton.

Studies of the influence of oxygen preadsorption on the course of interaction of unsaturated hydrocarbons with metal surfaces are interesting both from the point of view of catalyst poisoning and — in a generalized way — in modification of surface properties, namely in connection with the selectivity of catalysts. This paper deals with further investigation of the systems that were studied in our laboratory earlier, when both the simple interaction of hydrogen with oxygen bound to the metal surface<sup>1,2</sup> and the interaction between unsaturated hydrocarbons and the pure metal surface were investigated<sup>3-8</sup>.

## EXPERIMENTAL

Metal films were prepared in an all-glass apparatus<sup>3,9,10</sup> at pressures  $p \lesssim 10^{-8}$  Torr by condensing the evaporated metal onto a glass wall at 78°K. The films were thermally stabilized for about 60 minutes at  $\approx 350^\circ\text{K}$ . Amounts of gas were measured by means of McLeod manometers<sup>10</sup>, and the effect of thermal transpiration<sup>3,10-12</sup> was taken into consideration. Kinetic measurements were carried out using a thermal conductivity manometer.

Cyclopropane (ICI, England, for medical purposes) and propylene (from a tank) were purified by repeated condensation and by pumping away at 78°K prior to each experiment. Hydrogen was obtained by electrolytic decomposition of water and purified by diffusing through a palladium tube. Oxygen was prepared by thermal decomposition of  $\text{KMnO}_4$  and purified by passing it through a liquid nitrogen cooled trap. Inert gases used in determination of surface areas of films were supplied in glass ampules by Norsk Hydro (Kr) and Messer Griesheim, Düsseldorf (Xe). "Cathode" nickel was used as a source material for evaporating (99.8% Ni, 0.2%  $\text{SiO}_2$ , MgO),

its adsorption properties did not differ from those of spectroscopically pure nickel<sup>13</sup>. Platinum was obtained from Johnson, Mathey, Co., England.

## RESULTS

Surface areas of evaporated films varied from experiment to experiment. To make the comparison of the results possible, all measured quantities were related to the same area unit. A measure of the surface area was a monomolecular adsorbed layer of Kr (or Xe) at 78°K as determined by the BET method. However, this quantity is no physical constant characterizing the film, but depends rather on the state of its surface. Over a given film, the value of the monomolecular coverage always decreased

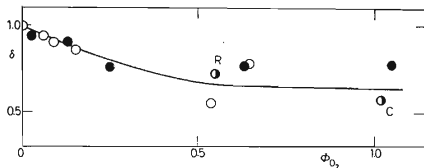


FIG. 1

Dependence of the Extent of Inert Gas Monolayer  $\delta$  on the Amount of Preadsorbed Oxygen  $\phi_{O_2}$

Both quantities related to the original value of the inert gas monolayer over a clean surface;  $\delta = N_i^m / (N_i^m)_c$ ,  $\phi_{O_2} = q_{O_2} / (N_i^m)_c$ ;  $\circ$  Pt surfaces measured by means of Xe;  $\bullet$  Ni surfaces measured by means of Kr; the point denoted „R“ is Fe surface measured by means of Kr<sup>15</sup>, the point „C“ is Ni surface measured by means of Kr<sup>14</sup>.

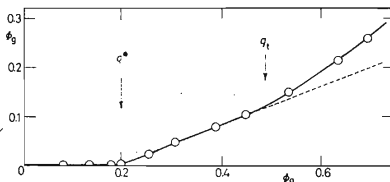


FIG. 2

Dependence of the Amount of Gas which Appears in the Gaseous Phase after the Chemisorption of Individual Propylene Portions on a Ni Film Partially Covered by Oxygen ( $\phi_{O_2} = 0.25$ ) at Room Temperature

$q_g$  amount of residual gas;  $q_a$  amount of propylene admitted;  $\phi_{O_2} = q_{O_2} / (N_{Kr}^m)_c$ ;  $\phi_g = q_g / (N_{Kr}^m)_c$ ;  $\phi_a = q_a / (N_{Kr}^m)_c$ .

after the chemisorption of studied gases (oxygen, cyclopropane, propylene) was performed, in comparison with the value for a clean surface. For oxygen the extent of the monomolecular layer of Kr (Xe) gradually decreased with the increasing amount of preadsorbed oxygen<sup>7,8,14,15</sup> (Fig. 1). Therefore, all measured quantities were related to a unit of the original area of the clean film (expressed in moles of Kr or Xe adsorbed in a monomolecular layer).

If an unsaturated hydrocarbon is admitted in small portions over a surface of the metal which is either clean or covered with preadsorbed oxygen, the amount of gas which remains from each portion in the gaseous phase,  $q_g$  (either not consumed or desorbed after an interaction with the surface) can be measured as a function of the total amount added,  $q_a$  (Fig. 2). The first portions of the gas are chemisorbed practically instantaneously and without any amount left in the gaseous phase. After the surface has been covered by the chemisorbed layer to a certain extent,  $q^*$ , the selfhydrogenation takes place<sup>3,4,16,17</sup>. This means that those hydrogen atoms whose bond with the carbon skeleton weakened or dissociated, are able to react — from this coverage up — with further added hydrocarbon molecules to form saturated hydrocarbon molecules subsequently released into the gaseous phase. This critical coverage  $q^*$  manifests itself by a well defined break on the curves, and represents a characteristic quantity for a given system<sup>4</sup>. The line slope  $P$  from the point  $q^*$  (Fig. 2) shows how many molecules appear in the gaseous phase after one molecule of the unsaturated hydrocarbon reacted with the surface (assuming all gaseous molecules have interacted with the surface earlier). The rate of reaching a stationary state decreases at larger total amounts of gas added and gradually longer time intervals are needed to reach this state. At the later stages this causes a gradual bending of the curve toward a limit close to  $P = 1$ ; this would correspond to a situation where no further interaction of the added molecules with the surface occurs. In the curvature region one can approximately determine the value of the total coverage of the surface by the adsorbed molecules,  $q_t$  (e.g. by a linear extrapolation of the two branches of the curve). No analysis of products on the gaseous phase over the modified surfaces was available in this work. However, interesting information was obtained showing how the oxygen preadsorption influenced the values  $q^*$ ,  $q_t$ ,  $P$ , and the rate of reaching the stationary state when individual portions of hydrocarbon were added. A rough information concerning the final products was obtained by freezing out the gaseous phase over the adsorbent at 78°K; in this way the condensable and non-condensable fractions of the products were distinguished.

#### *Platinum–Oxygen–Cyclopropane System*

Measured values of some of the above mentioned quantities are summarized in Fig. 3. It follows from these results and from earlier kinetic studies made in this laboratory<sup>7</sup> that in these processes at least two mechanisms take place while the surface is being

covered with oxygen. It is substantial that in two regions of coverage (initial and final) a non-condensable fraction of products (about 30%) appears in the gaseous phase. This fraction is presumably carbon monoxide or methane, as a mere replacement of the surface oxygen or hydrogen is — to such an extent — improbable. This indicates that the carbon skeleton remains intact over pure platinum, but that it desintegrates over the platinum surface partially covered with oxygen. If the non-condensable product is carbon monoxide (some results published on an analogous system Pd-O<sub>2</sub>-C<sub>2</sub>H<sub>4</sub><sup>17</sup> support this assumption), then the results indicate that oxygen is at least partly reactive and interacts directly with the hydrocarbon.

### Nickel-Oxygen-Propylene System

The system nickel-oxygen-cyclopropane was not investigated in this study, as even on a clean nickel surface its selfhydrogenation is complicated by cracking processes<sup>4</sup>.

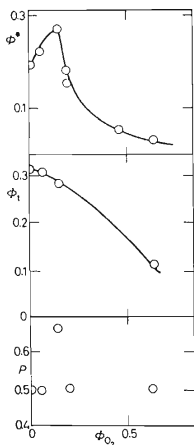


FIG. 3

Dependence of  $\phi^* = q^*/(N_{Kc}^m)_c$ ,  $\phi_t = q_t : (N_{Kc}^m)_c$ , and  $P$  for Cyclopropane on the Amount of Preadsorbed Oxygen  $\phi_{O_2} = q_{O_2}/(N_{Kc}^m)_c$

Measured at room temperature over platinum.

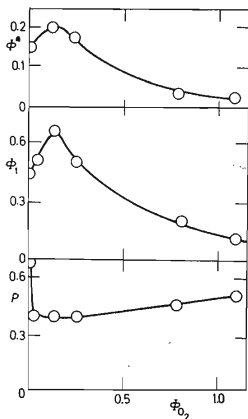


FIG. 4

Dependence of  $\phi^* = q^*/(N_{Kc}^m)_c$ ,  $\phi_t = q_t : (N_{Kc}^m)_c$ , and  $P$  for Propylene on the Amount of Preadsorbed Oxygen  $\phi_{O_2} = q_{O_2}/(N_{Kc}^m)_c$

Measured at room temperature over nickel.

In our experiments when no detailed analysis of the gaseous phase was available, it appeared more convenient to work with propylene which does not crack on the clean nickel surface<sup>18</sup>.

Fig. 4 summarizes results of measurements of the quantities  $q^*$ ,  $q_1$ , and  $P$  as a function of the preadsorbed oxygen amount for the nickel–oxygen–propylene system. In this case the non-condensable fraction (at 78°K) was negligible (less than 5%). Thus, it may be concluded that oxygen on the nickel surface is less reactive; at least no extensive oxidation occurs, as it does over platinum. However, the effect of preadsorbed oxygen does not manifest itself by a mere surface blocking (see  $q^*$  in Fig. 4). The course of the dependence  $q^*$  (the amount of propylene – or cyclopropane – chemisorbed without selfhydrogenation) upon  $q_{O_2}/(N_{Kr}^m)_c$  or  $q_{O_2}/(N_{Xe}^m)_c$  was the same for both nickel and platinum ( $q_{O_2}$  is the amount of preadsorbed oxygen,  $(N_{Kr}^m)_c$  and  $(N_{Xe}^m)_c$  is a monolayer of krypton or xenon, respectively, over the clean metal surface). It exhibited a maximum in the region of low oxygen coverage. This indicates an analogous role of preadsorbed oxygen in the early stages of the reaction on both metals.

## DISCUSSION

The interaction of hydrogen with oxygen over the surface of transition metals (Ni, Mo, Rh, Pt, Pd) was studied at the room temperature<sup>1,2</sup>. The differences in their activity that were observed hang together both with the reactivity of the original system (metal–oxygen–hydrogen), and with the types of products formed (H<sub>2</sub>O or OH) and their bonding to the surface<sup>1,2</sup>. According to the behaviour in this reaction, the studied metals could be divided into two groups: those over which the reaction products are only weakly bound so that the reaction can be repeated several times (*e.g.* Pt, Pd), and those over which the reaction does not take place – under the conditions studied – at all (Mo) or takes place solely over the virgin surface and cannot be repeated (Ni)<sup>1,2</sup>. It is very probable that this result may be explained

rather by the difference in the quality of reaction products (H<sub>2</sub>O on Pt, Pd, Rh, and OH on Ni) than by the difference in the adsorption bond strength of one single product (H<sub>2</sub>O)<sup>1,2</sup>.

Similarly as in the reaction of hydrogen with oxygen, two types of interaction could be distinguished in the study of the chemisorption of cyclopropane over the transition metals (Pt, Pd, Rh, Ni, Mo, Fe)<sup>4</sup>: platinum and palladium can split only C–H bonds so that propane is the only gaseous product of chemisorption, while nickel, molybdenum, and iron (at 320°K) yielded – as gaseous products of selfhydrogenation – also saturated hydrocarbons lower

TABLE I  
Dissociation Energies of Bonds  
with Hydrogen

Bond	kcal/mol
H–H	103
HO–H	116
O–H	103
H <sub>2</sub> C=CH–H	<121
C <sub>3</sub> H <sub>7</sub> –H	100

than  $C_3$ . In another words, splitting of C—C bonds of the original skeleton occurred.

Both reactions mentioned in the preceding paragraphs have one feature in common: formation or dissociation of a bond between hydrogen and another particle. As far as reaction energetics is concerned, both reactions should be rather similar (Table I) (ref.<sup>19</sup>), and thus it is not surprizing that the behaviour of these metals is analogous as far as the H-atom transfer is concerned. Moreover, in the case of hydrocarbons the specific ability of metals to split the carbon skeleton may take place.

If oxygen preadsorption is followed by chemisorption of cyclopropane (or propylene), a new partner is added to the surface which competes for hydrogen atoms with the chemisorbed molecules and/or hydrocarbon fragments. The reported results show that the presence of oxygen at the beginning in effect increases the "space" for the "labile" hydrogen presumably by forming a bond with it (probably in a similar way as, *e.g.*, nickel surfaces partly covered with oxygen chemisorb at the room temperature several times more hydrogen than the clean surfaces)<sup>2</sup>. This, naturally, suppressed selfhydrogenation, *i.e.*  $q^*$  increases. Further course of interaction, when increasing the amount of preadsorbed oxygen, then obviously depends on the kind of metal over which the reaction takes place. Over the nickel surface a relatively stable complex NiOH is presumably formed so that oxygen is strongly bound to the surface and appears in this sense as "non-reactive". However, over platinum oxygen is able to react partly both with hydrogen to form water (collected in traps) and with the carbon skeleton to form presumably carbon monoxide and carbon dioxide. Further increasing of the amount of preadsorbed oxygen leads then to blocking the surface as far as hydrocarbon adsorption is concerned. As a result, the value of  $q^*$  decreases.

Thus, preadsorbed oxygen essentially changes the mechanism of interaction between metals and unsaturated hydrocarbons: 1. it influences the transfer of hydrogen from one hydrocarbon molecule to the other; 2. it reacts directly with the carbon skeleton (see platinum). As the composition of the products of both selfhydrogenation and hydrogenation (as proved for systems cyclopropane-transition metals<sup>4</sup>) is the same, both these effects might be of practical importance in modifying metal surfaces either for selective hydrogenation (dehydrogenation) or for selective oxidation.

An analogous result, *i.e.* the dependence of  $q_t$  on the amount of preadsorbed catalytical poison ( $CO_2$  in this case) exhibiting a maximum, was observed by Hirota<sup>20</sup> for the system nickel-carbon dioxide-ethylene. However, no detailed interpretation of this effect was given by the author.

Recent results of studies of redox reactions over oxides<sup>21</sup> have shown that hydroxyl groups (or the presence of hydrogen atoms) influence the selectivity of these reactions to a considerable extent. The above mentioned results indicate that a similar mechanism may take place in redox reactions over metals partially covered with oxygen.

*In conclusion, the authors would like to express their thanks to Academician R. Brdička for his interest in this and all the preceding works in the Institute of Physical Chemistry, Czechoslovak Academy of Sciences. Many helpful discussions with Dr R. Merta are gratefully acknowledged.*

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