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ON THE MOLECULAR MECHANISM OF CATALYTIC OXIDATION OF OLEFINS

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In every oxidation reaction two reactants take part: oxygen and the molecule to be oxidized. The reaction may thus start either by activation of the dioxygen (electrophilic oxidation) or by activation of the hydrocarbon molecule (nucleophilic oxidation). The surface of an oxide catalyst for selective oxidation must thus be tailored to perform a complex multistep operation on the reacting molecules, at the same time hindering those interactions that could lead to unwanted byproducts.

A theoretical description of chemical reactions may be attempted on the basis of the concept of the potential energy hypersurface for molecular motions. The minima on such a hypersurface correspond to stable systems; i.e., to reactants and products of the reaction network investigated. As the networks for the oxidation of hydrocarbons on oxide surfaces are relatively large systems, even the semiempirical computation is time-consuming and further simplifications of the model must be adopted to make full description feasible. Analysis of experimental data suggests that as the form of the transition state is already determined at the preliminary stage of the reaction, the energy gradient estimated from the difference of total energies at two points chosen at relatively large distances between the reactants may be taken as an indication of the potential barrier encountered on approach from a given direction. Thus, reaction pathways characterized by the lowest energy barriers may then be analyzed.

Calculations were carried out for the reaction pathways in the system composed on non-activated and activated butene interacting with molecular or atomic oxygen. A general conclusion may be formulated that the important functions of active centers of the oxidation catalyst consist in the adsorption of the reacting molecules in the appropriate mutual orientation and in modification of their relative electrophilic-nucleophilic character.

Keywords: Butane oxidation, oxide catalysis, molybdenum oxide catalysts

1. Introduction

Oxide surfaces usually contain active sites which can interact with reactants of catalytic reactions by exchanging electrons as well as protons or oxide ions, and therefore may play the role of catalysts in both redox and acid-base reactions [1–3]. When the reacting medium is composed of a mixture of hydrocarbon and oxygen molecules, the reaction may start either by activation of the dioxygen or by activation of the hydrocarbon molecule and usually may follow various reaction pathways, giving a number of different products. By developing a

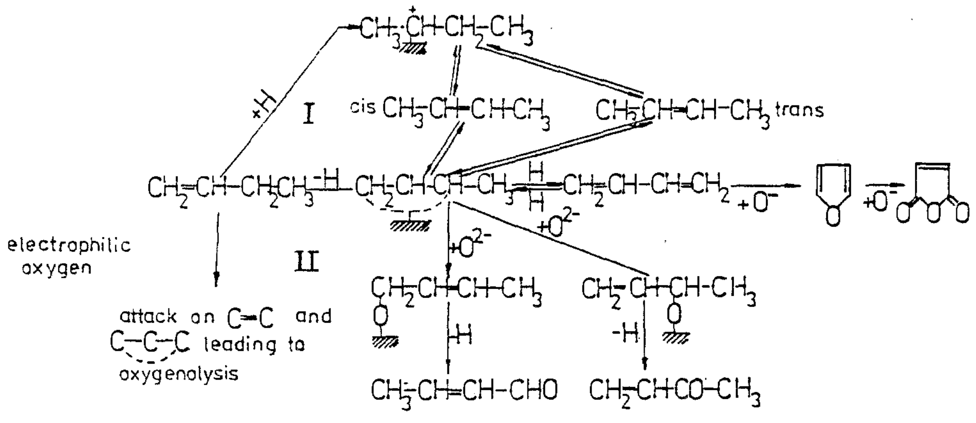


Fig. 1. Reaction network of butene-1 at the surface of an oxide catalyst.

catalyst which would accelerate the reaction along only one of these pathways, very often thermodynamically not the most convenient one, formation of a product becomes possible, which otherwise would have never been obtained because of the much more rapidly proceeding competitive processes. Thus, tailoring of a selective catalyst requires generation of active sites involved in the sequence of consecutive elementary steps transforming the initial reactants into the desired products and elimination of those sites, which could divert the reaction along the pathways leading to unwanted products.

As an example fig. 1. shows the reaction network of butene-1 and oxygen at the surface of an oxide catalyst. On interaction of butene-1 molecule with the Brönsted acid site a carbocation is formed which starts an easy route of double bond shift and cis-trans isomerization [4]. The presence of Lewis sites, e.g. empty d-orbitals of transition metal ions gives rise to binding of the olefin through its π-electrons into a surface π-complex. When the basicity of surface oxide ions O^{2-} is high enough, the proton in the α-position to the double bond may be abstracted and an allyl species may be formed [5]. Repetition of this step with the proton at C4 now in α-position to the allylic group, results in the formation of butadiene. Depending on the electronic properties of the oxide a transfer of electrons takes place between the surface and the allyl species. If the latter acquire a positive charge they become prone to a nucleophilic attack of surface O^{2-} ions, which may attach to the terminal carbon atom giving croton aldehyde, or to C3 atom forming methyl vinyl ketone. This represents the nucleophilic oxidation route [6].

Simultaneously, many different surface sites may play the role of sites activating oxygen molecules to various reactive adsorbed species of electrophilic character, e.g. singlet oxygen, molecular radical O_2^- or atomic radical O^-. They may be generated at surface vacancies acting as F-centers, transition metal ions characterized by several near lying oxidation states etc. The electrophilic oxygen

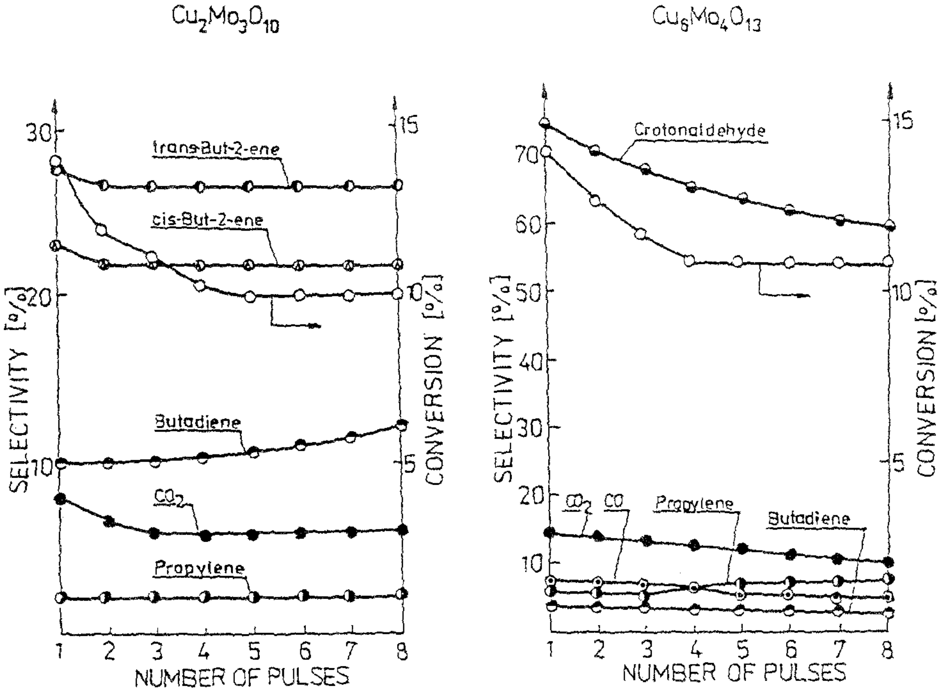


Fig. 2. Conversion and selectivities to different products as a function of the number of pulses of butene-1 on $Cu_2Mo_3O_{10}$ and $Cu_6Mo_4O_{15}$ catalysts at 370 ° C.

species may react with butene, all intermediates and products forming a network of parallel-consecutive reactions, which either lead to oxygenolysis or to the formation of acids and anhydrides in–what is called–electrophilic oxidation route [7].

One of the very versatile catalytic systems, which is also known to be active in butene isomerization is MoO_3 [8]. Impregnation with Bi^{3+} or addition of Bi_2O_3 to form bismuth molybdate generates a catalytic system active and selective in oxidative dehydrogenation of butene to butadiene [9]. When copper oxide instead of bismuth oxide is reacted with MoO_3, a catalyst is obtained for the oxidation of butene to croton aldehyde [10,11]. It is interesting to note that copper-molybdenum oxide catalyst represents a most spectacular example of the strong influence of surface structure on the selection of the reaction pathway by the hydrocarbon-oxygen reacting system. Cu_2O forms with MoO_3 two cuprous molybdates: $Cu_2Mo_3O_{10}$ and $Cu_6Mo_4O_{15}$ [12]. Both are composed of the same chemical elements in the same valence states and differ only in the spatial arrangement of atoms. Yet, as illustrated by fig. 2, they show entirely different catalytic properties: $Cu_2Mo_3O_{10}$ is active in the isomerization and oxidative dehydrogenation, but no traces of oxygenated hydrocarbon molecules are present in the products, whereas $Cu_6Mo_4O_{15}$ mainly inserts oxygen into the organic molecule to form croton aldehyde. The most striking feature is the complete absence of isomerization in the latter case. Moreover, when divalent copper molybdate $CuMoO_4$ containing excess of MoO_3 is reduced in situ in the reactor by pulses of butene-1, methyl vinyl ketone begins to build up in the products, its selectivity attaining 20% [11]. Methyl vinyl ketone is formed from butene with high yield also on copper oxide catalyst [13]. In the case of MoO_3-V_2O_5-P_2O_5 system used as catalyst, butene-1 is oxidized further to maleic anhydride [14].

It may be seen that modification of the catalyst composition or variation in its crystal structure can modify its catalytic properties to such an extent that the direction of the reaction is changed and a new product appears, usually with high selectivity. A fundamental question may be raised as to which parameters decide that the reacting system selects a given pathway out of many possible ones.

This subject has a direct bearing upon the fundamental problem of catalysis and concerns the role of steric and electronic factors imposed upon the reacting molecule by their interaction with the surface of the catalyst, in determining the selectivity of the catalytic reaction.

One of the theoretical descriptions, which may be attempted in order to discuss the problem of choosing the reaction pathways which lead to desired products, bases upon the concept of the potential energy surface [15–17].

The reaction pathway is a curve on a multidimensional potential energy surface (PES), which connects minima and passes through saddle points. In any point the reaction path is perpendicular to the isoenergetic curves i.e., the reaction pathway is the steepest descent path when going from the saddle point to the minima. The minima on the PES represent reactants, products and intermediates. The first order saddle point is associated with active complex (transition state).

The reaction coordinate, usually considered as synonym of the reaction pathway, is a one dimensional representation of the reaction path, e.g., a measurable curve along the reaction pathway. The detailed understanding of the mechanism of chemical reaction requires a knowledge of PES, which must be determined point by point by quantum chemical methods because, in general, it is not available analytically. The construction of PES is a difficult and time consuming procedure specially when a system of large size is under consideration as it is usually the case in catalysis. This is due to the necessity of evaluation of an energy grid containing n^v points, where v is the number of variables on which the energy depends and n is the number of values of each variable required to characterize the PES.

There are several methods to reduce the dimensionality of the problem. One of them allows to limit the calculations to only those reaction pathways which are characterized by the lowest energy barriers and what follows which are assumed to be the most probable. The choice of such a reaction pathway may base on the form of the potential energy surface at large distance between the reactants [18]. This assumption follows from the experimental data, which suggests that the form of the transition state is predetermined already in the preliminary stage of the reaction. The energy gradient evaluated from the difference of the total energies at two arbitrarily chosen points on the reaction coordinate at relatively long distances between the reacting molecules, may serve as the indication of the potential energy barrier encountered on approach from the given direction.

It seemed therefore of interest to apply this approach to the model systems composed of various oxygen species approaching from different directions butene-1 or its activated allylic form and to calculate the changes of the total energy and of the bond length in the course of the reaction.

The calculations were performed using MNDO quantum chemical method; the program contained a procedure for locating minima on MNDO potential surface by means of DFP algorithm [19–21]. The interaction with the catalyst were not explicitly included, but its presence was accounted for by repeating the calculations for several total numbers of electrons in the system in order to take into consideration the fact that during the catalytic process the transfer of electrons from or to the surface of the catalyst may occur. The operation of the catalyst was also implicitly included by performing the calculation for the systems composed of allylic species, which are generated at the catalyst surface.

In order to select the most probable reaction pathways simple energy maps were constructed in such a way that total energies of the system built of an oxygen species and butene-1 or its allylic form, for two distances between reactants were calculated, with the frozen geometry of subsystems. Calculations of energy of the system along reaction pathways including full geometry optimization were carried out only for those directions of the attack of oxygen moieties on particular sites in hydrocarbon species which were selected on the basis of the potential energy maps.

2. Results and discussion

Let us start from the discussion of the attack of molecular oxygen on a non activated butene molecule. The energy maps indicate only one direction of the attack which is expected to proceed with relatively low energy barrier. It is the attack from above the plane of butene-1 onto the C1=C2 double bond (the axis of O_2 molecule parallel to the double bond) [22].

Fig. 3 summarizes the reaction pathways followed in the attack by O_2 (fig. 3a) and O_2^- (fig. 3b) moieties. The attack of both species onto the C1=C2 double bond results in the scission of this bond and formation of methanal and propanal molecules as products. The shape of the reaction pathway for these two cases is however quite different. The attack of O_2 molecule encounters a very high energy barrier, arising from the necessity of simultaneous elongation and cleavage of two double bonds, O=O and C=C. The attack of O_2^- ion requires much lower energy because the O–O bond is already elongated and, what follows, weaker. The local minimum corresponds to the end-on addition of oxygen species to C1 atom. This intermediate easily reconstructs and forms bridge-like transition state in which oxygen molecule is bonded to two carbons, C1 and C2 forming a peroxo bridge.

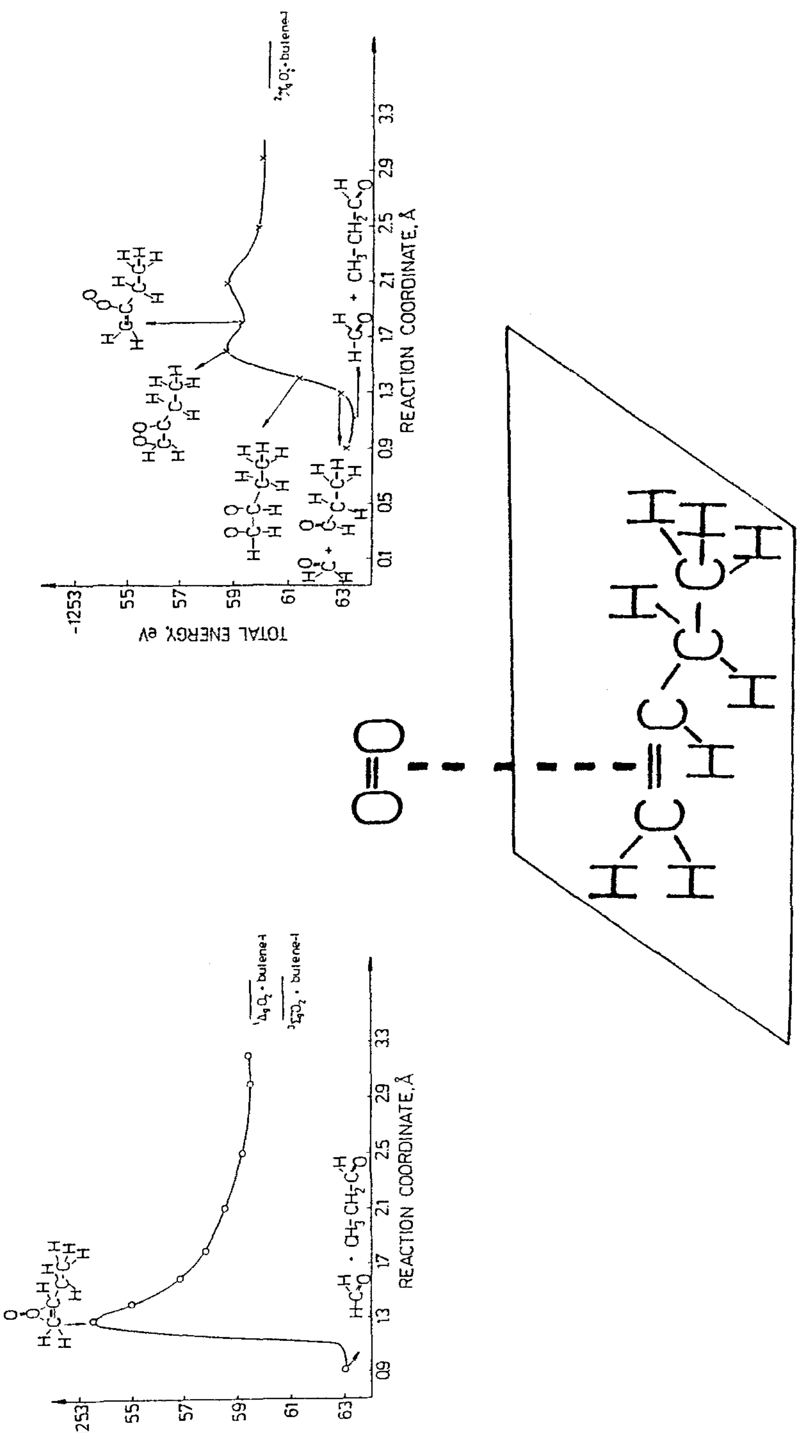


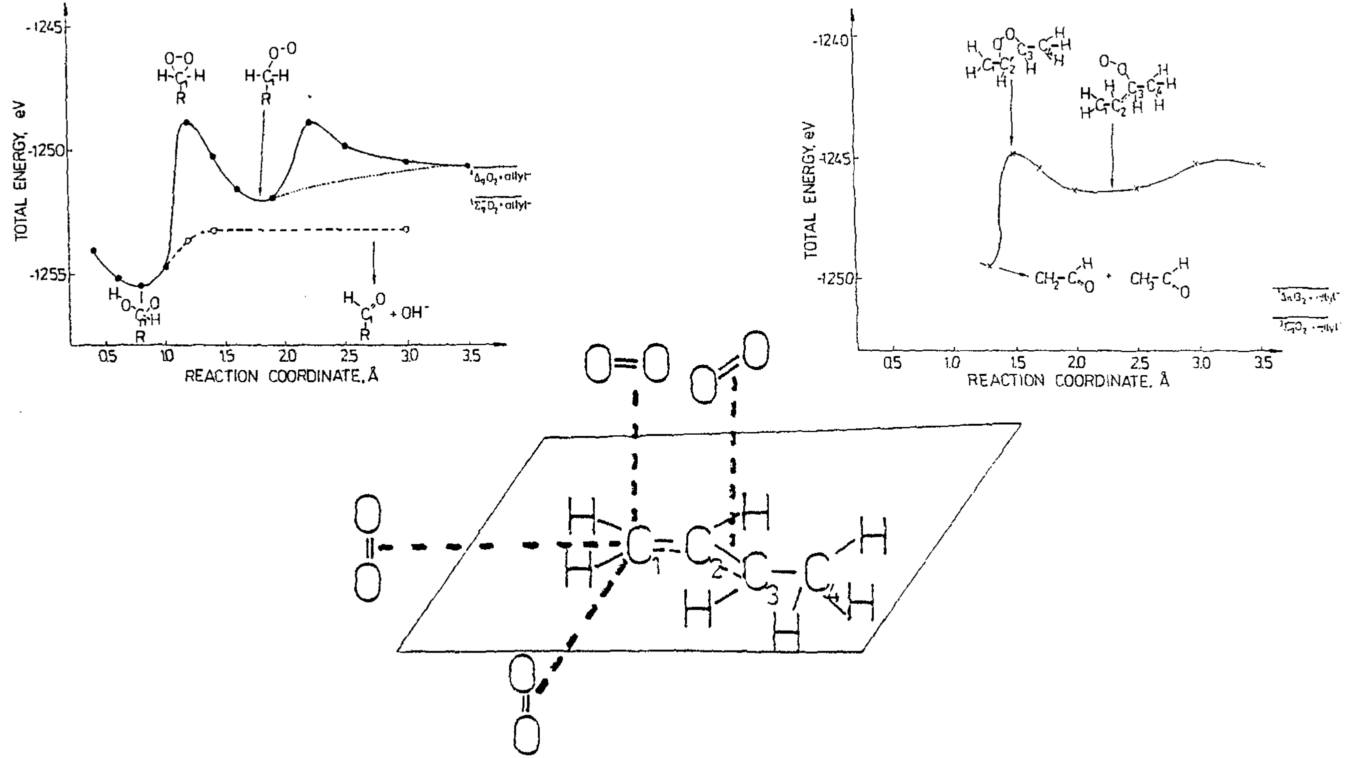
Fig. 3. Reaction pathways for the attack of molecular oxygen on a non-activated butene-1 molecule, a) attack of O_2, b) attack of O_2^-.

In the final step of the reaction–the cleavage of the two bonds takes place; as the first the O–O bond is broken, then the C–C bond is splitted. These two scission processes result in the formation of two molecules of aldehydes. When butene-2 is taken as the reactant, the electrophilic attack is directed on the double bond between C2 and C3 atoms, two molecules of ethanal being then formed as the results of the cleavage of peroxo bridge.

Let us pass to the attack of molecular oxygen on the butene molecule activated by abstraction of α hydrogen. The calculated energy maps indicate that the discussion of the oxidation reaction may be limited only to -1 charged system [22] and show that only the attack on C1 atom is expected to encounter relatively low energy barrier. The following routes of approach of oxygen molecule to allylic species are possible: (1). in plane attack along the C1–C2 bond axis, the oxygen axis perpendicular to the plane of allyl, (relatively low energy barrier); (ii). in plane attack along the direction perpendicular to the C1–C2 bond, the oxygen axis in plane, (relatively low energy barrier); and (iii). attack from above the plane (no energy barrier).

The attack from above the plane may proceed also on the C2–C3 bond. Fig. 4. represents reaction pathways for the different attacks of molecular oxygen on allylic species. The attack on C1 from above the plane as well as in plane along the axis of the C1–C2 bond leads to the same type of oxidized species. The reaction path (see fig. 4a) goes via local minimum associated with the formation of superoxo-type species (end-on addition of oxygen molecule to the C1 atom). This step encounters no energy barrier in the case of the attack from above the plane (dotted line). The energy barrier for the in plane attack on C1 (full line) arises from the steric hindrance caused by hydrogen atoms bonded to this atom. Starting from the local minimum both attacks are described by the same reaction pathway. The rearrangement of the system in the next step requires about 3 eV and leads to the transition state which is peroxo-type species (side-on addiditon of oxygen molecule to C1 atom). The final reorganization of the system consisting of the transfer of one hydrogen atom and formation of the OH group proceeds without any energy barrier. The appearing oxygenated species may be the precursor of either croton aldehyde or crotonic acid. The results of additional calculations for the process of the removal of OH group (formation of an aldehyde) or for the process of abstraction of H atom (formation of an acid), which were performed in order to answer the above question, indicate that the formation of croton aldehyde is energetically more favourable.

The reaction pathway for the in plane attack of molecular oxygen on C1, along the direction perpendicular to the C1–C2 bond, is demonstrated on fig. 4b. The shape of the pathway as well as the types of species associated with the local minimum and with the transition state are similar to the previously discussed case. The difference in the type of product formed, which is an anion of crotonic acid, arises from the fact, that in this case both hydrogen atoms bonded to C1 atom are close to each other and are abstracted in the form of hydrogen molecule.


TOTAL ENERGY, eV
-1245
-1250
-1255
0.5
1.0
1.5
2.0
2.5
3.0
3.5
REACTION COORDINATE, Å
O-O H-C-H R
O-O H-C-H R
H-O-C-O H R
H-C-O R + OH⁻
Δ$_g$O$_2$+allyl⁻
Σ$_g$O$_2$+allyl⁻
TOTAL ENERGY, eV
-1240
-1245
-1250
0.5
1.0
1.5
2.0
2.5
3.0
3.5
REACTION COORDINATE, Å
CH$_2$-C(H)O + CH$_3$-C(H)O
O=O
C$_1$
C$_2$
C$_3$
C$_4$
H

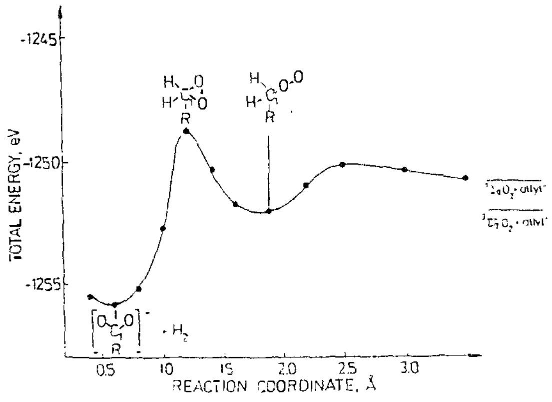


Fig. 4. Reaction pathways for the attack of molecular oxygen on activated butene-1 i.e. on allylic species, a) attack on C1 (full line corresponds to the eri-plane attack along C1–C2 bond; dotted line to the attack from above the plane), b) attack on C1 (eri-plane, perpendicular to C1–C2 bond), c) attack from above the plane on C2–C3 bond.

The attack of molecular oxygen on C2–C3 bond from above the plane is presented on fig. 4c. The first local minimum is connected with the end-on addition of oxygen molecule to C3 atom. After rearrangement which costs only about 1.5 eV the bridge-like oxygenated species is formed with oxygen molecule bonded to C3 and C2 atoms. In the last step of the reaction, the simultaneous cleavage of C2–C3 and O–O bonds takes place and the two molecules of ethanal are formed as products (one with the lack of one hydrogen atom). In all discussed cases the distance between the middle of O–O bond and C1 atom or the middle of C2–C3 bond was taken as the reaction coordinate. One has to mention that at large distances the extra electron locates itself on allylic-like species so, in fact, the attack of molecular oxygen on allylic anion was studied.

Let us finally consider the reaction between the activated butene molecule and atomic oxygen species. The results of calculations of the energy maps indicate two directions of the attack of oxygen onto allyl for which the energy gradients have negative values and along which the reactions can proceed without the energy barrier. Such situations happen for the attack from above the plane of allyl onto the C1 and C3 atoms for -1 charged systems fig. 5. Also the in plane attacks on C1 and C3, in case of -1 charged systems, proceed without the energy barrier fig. 5a. When atomic oxygen species approaches the C1 atom from above the allyl plane, the total energy of the systen decreases continuously, oxygen is added to carbon atom and after rearrangement the croton aldehyde like species is formed. Whereas on the in plane approach alcohol-like species is formed. Similar attacks on C3 proceed fig. 5b. along the reaction pathways of the same shape and lead without the energy barrier to the precursors of alcohol (in plane attack) or methyl vinyl ketone (attack from above the plane).

It is interesting, that the oxidation of C1 or C3 in case of -2 charged systems, proceeds directly to the desired products, i.e. to croton aldehyde and to methyl vinyl ketone, respectively for both directions of the attack. In these processes the negatively charged hydrogen is abstracted. Energetically both reactions require about twice as much energy as the processes for -1 charged systems. However it should be born in mind that the energy barrier may by considerably lower in conditions when the reaction takes place at the catalyst surface which interacts with both reactants.

Each of the processes producing the desired products directly may be split into two steps: formation of the precursors (in -1 charged system) and addition of extra electron to the precursors. Such a two steps reaction is energetically more favourable than the concerted process in -2 charged system.

One should mention that the oxidation of C1 and C3, in case of neutral systems, leads to appropriate alcohols, with the energy barrier equal to 2.8 and 2.3 eV, respectively.

Based upon the results of the calculations the following conclusions can be drawn:

- the course of oxidation process depends: on the preliminary activation of

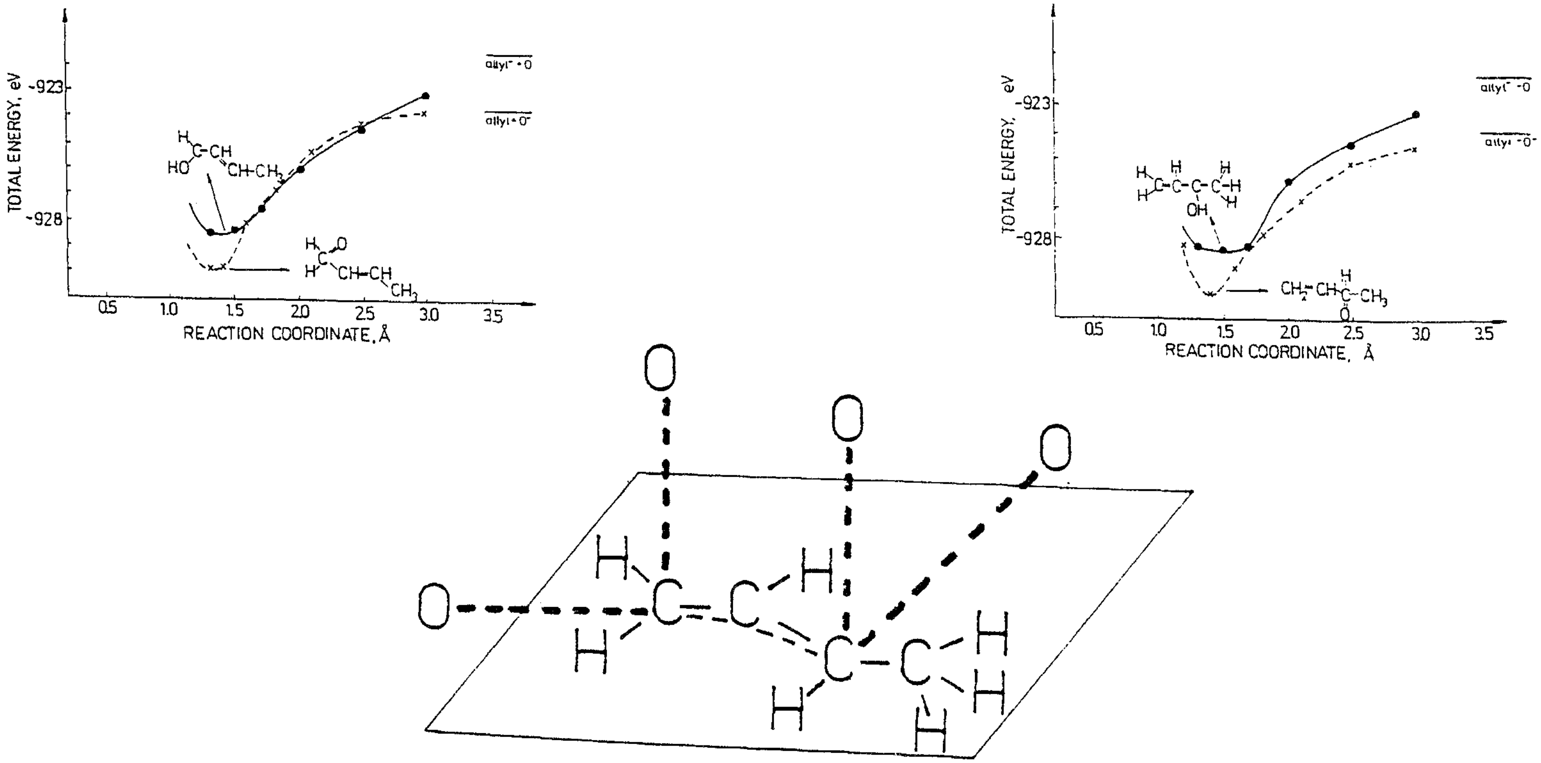


Fig. 5. Reaction pathways for the attack of atomic oxygen on activated butene-1 i.e. on allylic species, a) attack on C1 (full line corresponds to the eri-plane attack; dotted line to the attack from above the plane), b) attack on C3 (full line corresponds to the eri-plane attack; dotted line to the attack from above the plane).

the reactants (butene-1 or/and oxygen species) and on the mutual orientation of reacting molecules;

– the type of product depends on the site of oxygen attack; an attack on the double C=C bond results in the splitting of carbon skeleton and leads to the products of selective oxidation which have smaller number of carbon atoms in comparison to the initial reactant; an attack on the appropriate atoms proceeds via an addition of oxygen and gives the products of allylic oxidation e.g. the oxygenated species with the same as oxidized molecule number of carbon atoms.

– on the presence of an electrophilic oxygen species the oxidation reaction proceeds always according to the electrophilic mechanism independently of the preliminary activation of hydrocarbon molecule, i.e. an attach of oxygen is faster than the activation of hydrocarbon. The preliminary activation of hydrocarbon "opens" new sites (atoms) for electrophilic addition reaction.

The system composed of allyl species [C–C–C–C] and oxygen atom, and carrying a -1 charge, may be considered as built of $[\text{C–C–C–C}]^{1-}$ and O^0, $[\text{C–C–C–C}]^0$ and O^{1-} or $[\text{C–C–C–C}]^+$ and O^{2-}. Results of our quantum chemical calculations show that in such system oxygen atom, irrespectively of whether it approaches the allyl fragment in-plane or from above the plane, performs the attack on C1 or C3 atoms giving crotonaldehyde or methyl-vinyl-ketone respectively, the excess electron residing on the allyl species. Earlier calculations showed [23] that at the transition metal oxide surface the allyl species becomes positively charged due to the transfer of electrons from the allyl Π-orbitals onto the empty transition metal cation d-orbitals. The allyl cation thus formed at the surface is surrounded by O^{2-} oxide ions, which corresponds to the state of the system represented as $[\text{C–C–C–C}]^+$ and O^{2-}. It may be expected that such separation of charge induced by the interaction with the surface will considerably decrease the energy barriers on the reaction pathways shown in fig. 5 and the formation of crotonaldehyde or methyl-vinyl-ketone will be facilitated. These processes which may be considered as nucleophilic oxygen addition to the activated hydrocarbon molecule result in the selective formation of oxygenated products. They may be classified as nucleophilic oxidation [6]. In the presence of oxygen molecules which are characterized by electrophilic properties, another reaction pathway becomes more facile: the attack of oxygen molecule on the double bond of a non-activated butene molecule resulting in the formation of a peroxo bridge fig. 3, which is unstable and breaks into two oxygenated fragments. Such process may be called electrophilic oxidation. These two limiting cases may simultaneously appear when both reactants: olefin and oxygen molecules are activated at the catalyst surface. A complex reaction network begins then to operate.

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