

Quantum Chemistry and Catalysis in Oxidation of Hydrocarbons

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Catalysis is a phenomenon of increasing importance from both a theoretical and a practical point of view. The majority of technological processes used in the modern chemical industry are based on catalysis. With the world production of 3 billion tons of crude oil per year, the catalytic hydrosulfurization of petroleum is one of the largest technical operation in the world. Also most biochemical processes, vital for living organisms, are of catalytic type.

Heterogeneous catalysis is a phenomenon in which a relatively small amount of a solid, called the catalyst, increases the rate of a chemical reaction. The accelerating effect of a catalyst may be due to creation, through interaction with the substrates, of a new reaction path which is usually multistep and characterized by a lower energy barrier, or lifting of the symmetry restrictions in the case of concerted reaction.

The mechanism of catalytic reactions may thus be discussed in terms of the type of intermediate complex formed in the course of the reaction between the substrate molecule and the group of atoms at the surface of the solid, constituting the component of its lattice and called "active center". On interaction with such active centers, the electronic structure of the reacting molecule is modified, resulting in the rearrangement of chemical bonds and transformation of the molecule. Two basic questions must be answered: how bonding of the molecule in the intermediate complex modifies the electronic structure of this molecule and how this modification influences the reactivity of different bonds in the molecules and determines in this way the type of product formed in the course of the catalytic reaction. In recent years attempts have been made to answer

these questions on the basis of quantum chemical calculations.

Exact discussion of the process of chemisorption or catalytic reaction is not yet possible. Simplifications must be introduced in both quantum chemical methods and the structural models of the processes. The structural models can be classified (Figure 1)¹ as isolated molecule or molecules, quasi-isolated molecule, cluster, or semiinfinite and infinite crystal. In the case of homogeneous reactions, only the first two models are relevant. In the case of heterogeneous reactions, all four models are in use.

The present Account is based on the cluster model, although the advantages and limitations of various methods are illustrated by their applications in the description of the catalytic oxidation of hydrocarbons. Other presentations of the applications of quantum chemistry to surface phenomena are given in the reviews by Slater and Johnson,² Beran and Zahradnik,³ Beran et al.,⁴ Baetzold,⁵ Brenig,⁶ and Messmer.⁷

Catalytic Oxidation of Hydrocarbons

In the discussion of the role of intermediate complex in the catalytic reaction, three limiting cases are distinguished (Figure 2). From a given substrate the same intermediate complex may be always formed, but depending on the catalyst the potential barrier along different reaction coordinates is lowered and different products are thus formed. A second possibility is that depending on the catalyst different intermediate complexes are formed which then transform into different products. Finally, in a series of consecutive steps several intermediate complexes may form which either desorb to give one of the intermediate products or transform

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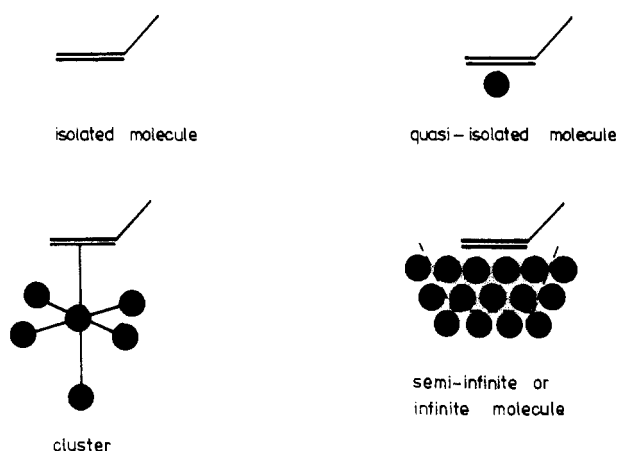
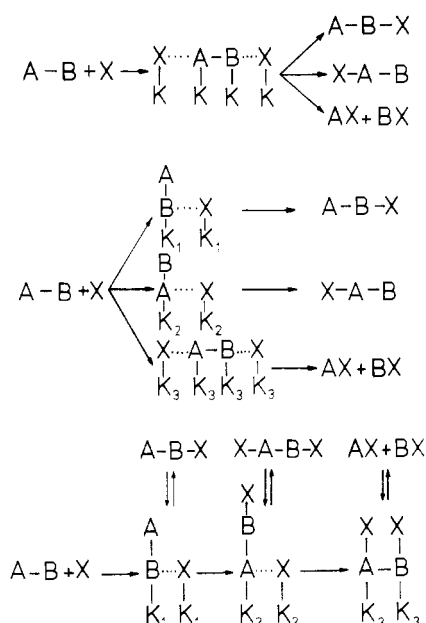
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Models simulating chemisorption and catalytic reactions

**Figure 1.** Models simulating chemisorption and catalytic reactions.**Figure 2.** Role of intermediate complex in determining the selectivity of the catalytic reaction.

consecutively into each other. Ample experimental evidence indicates that two different intermediate complexes between the reactants and the catalyst initiate two different paths of the reaction of catalytic oxidation of hydrocarbons,⁸ one resulting in total oxidation and the second leading to partial oxidation products (Figure 3).

When oxygen is activated at the surface of the catalyst and adsorbed in the form of ionic or molecular radicals O^- and O_2^- , the latter act as highly oxidizing species in the total oxidation of simple molecules such as H_2 , CO , CH_4 , etc. They may be considered as electrophilic reagents, which in reactions with olefin attack the molecule in the region of highest electron density. Such electrophilic addition of O_2^- or O^- results in the formation of peroxy or epoxy complexes, respectively, which in the condition of the heterogeneous catalytic oxidation are intermediates of the degradation of carbon skeleton and total oxidation.

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The reaction path leading to partial oxidation may be considered⁸⁻¹⁰ as a series of consecutive steps each of them consisting of one elementary transformation of the reacting molecule and formation of a different intermediate complex. In the case of the oxidation of olefins, the following steps have been suggested. First, activation of the olefin molecule, consisting of the abstraction of α -hydrogen and formation of π -bonded allylic species, taken place on cationic active centers. In the case of such catalysts as molybdates, tungstates, etc., these centers involve oxygen polyhedra of such cations as Bi^{3+} , Co^{2+} , Ni^{2+} , etc. When no other centers are present at the surface, the π -allyl species recombine to give dimers of diene type or form polyenes by repetition of the first step on cationic active centers. This process is favored when no charge is present on terminal carbon atoms of the activated species. Different active centers at catalyst surface are required for the insertion of oxygen. Oxygen polyhedra of molybdenum, tungsten, etc., are involved in creation of these centers, on which the allylic species transform into allyl species σ -bonded to lattice oxygen ions of these centers. They may then desorb in the form of aldehyde, leaving an oxygen vacancy on the surface of the catalyst. The nucleophilic attack of oxygen on the allylic species is facilitated when positive charge appears on its terminal carbon atoms. A third type of active center is involved in the insertion of a second oxygen atom into the organic molecule, resulting in the formation of a carboxylate intermediate complex, which then desorbs in the form of acid.

These mechanistic features of olefin oxidation raise a number of interesting questions. Four important ones are the following: (1) Which properties are required for the active centers to abstract the hydrogen atom from the olefin molecule and generate the allylic species? (2) How does the charge on the terminal carbon atoms of the adsorbed allylic species depend on the properties of the active center? (3) Which properties of the oxide are responsible for its ability to insert oxygen into the organic molecule by nucleophilic attack? (4) What is the mechanism of the insertion of a second oxygen atom and transformation of an aldehyde group into a carboxylic one. We examine these questions using semi-empirical quantum calculations in the following section.

Theoretical Calculations

In order to answer the first of these questions, SIN-DO quantum-chemical calculations have been carried out of the interaction of propylene with the surface of oxide catalyst.¹¹ The complex consisting of cobalt (or magnesium) ion, five oxygen atoms, and the propylene molecule as the sixth ligand has been used as a model of the catalyst surface. Figure 4 shows the total energy as a function of the distance of propylene molecule from the plane of cobalt complex. A minimum of this function corresponds to the formation of a stable intermediate surface complex. The dotted line represents the changes of total energy of the system when not the whole propylene molecule but only the allylic species is being removed away from the surface in the perpendicular direction, one hydrogen atom remaining at the surface. Apparently, this process is energetically

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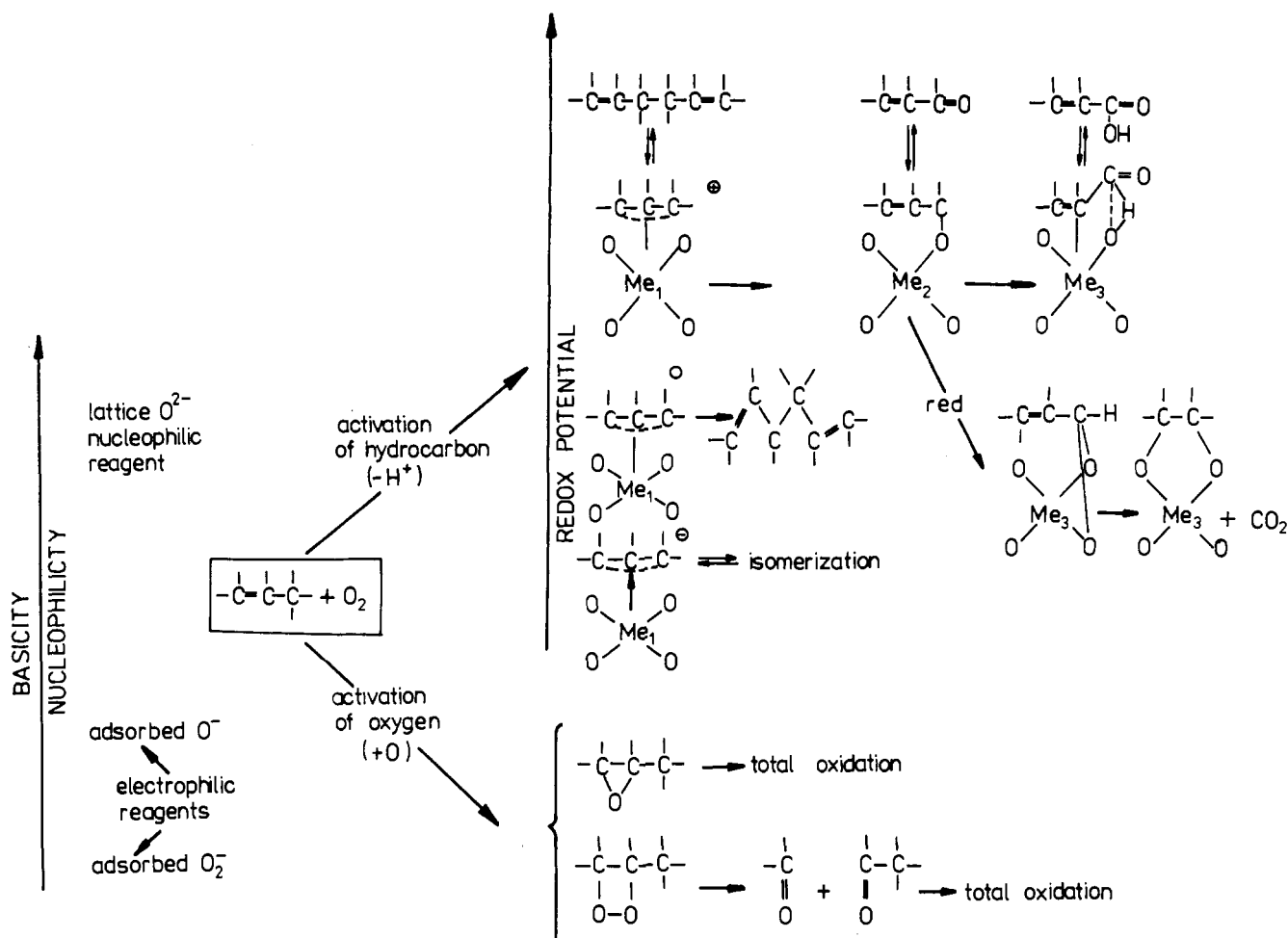


Figure 3. Mechanism of the catalytic oxidation of hydrocarbons.

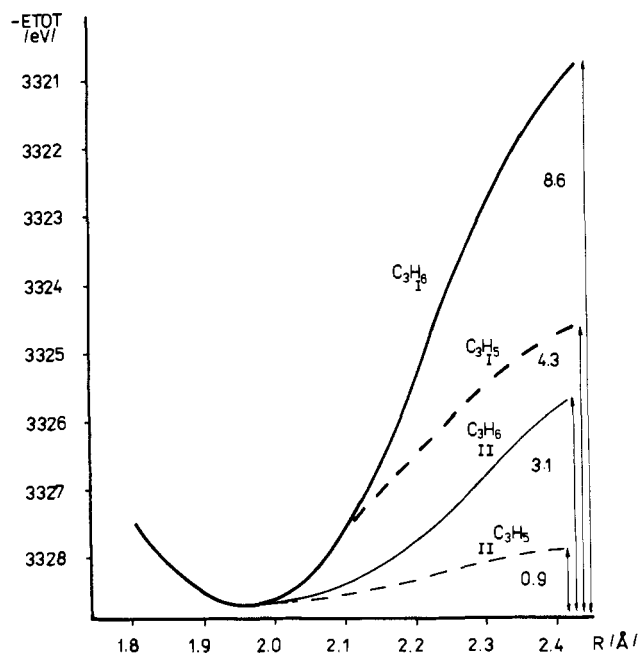


Figure 4. Total energy as a function of the distance of propylene molecule and allyl species from the plane of the cobalt complex. Curve I corresponds to SINDO energy; curve II corresponds to SINDO energy + Madelung correction.

much more favorable than removal of propylene. A strong interaction of α hydrogen from the propylene molecule with surface oxygen atom leads to CH bond

splitting. Thus it may be concluded that on contacting propylene with the surface of cobalt oxide, its reactive chemisorption takes place, resulting in the formation of an adsorption complex with allyl species as one of the ligands.

The next problem is the dependence of the ability to activate the hydrocarbon molecule on the properties of the cation at the catalyst surface. When discussing the properties of the intermediate complex in heterogeneous catalytic reaction it is necessary to take into account the fact that complex is a constituent of the surface of the solid. In the isolated complex the total number of electrons is simply the sum of the number of electrons of the atoms in the complex and is thus fixed. On the other hand, for a complex at the surface of a solid the total number of electrons in the complex is determined by the chemical potential of electrons in the solid given by the position of the Fermi level and may change when its position changes. It is not possible to determine directly the relative position of the energy levels of the surface complex and the Fermi level of the given solid. The influence of the change of the Fermi level position on the properties of the complex may be studied, however, by performing the SINDO calculation at varying numbers of electrons in the complex. Figure 5 shows the total energy of the complex (curve I) and the difference of diatomic contributions to the total energy, $\Delta = E_{OH} - E_{CH}$ (curve II), as a function of the total number of electrons in the cobalt complex. The total number of electrons in the isolated complex amounts

Table I
Results of SCCC MO calculations

metal	no. of unpaired electrons in complex	av no. of π electrons on allyl	populations in allyl orbitals			charge on carbon atoms (in e units)			
						terminal		central	
			π_1^b	π_2^n	π_3^a	π -electronic contribution	total charge	π -electronic contribution	total charge
	1	3	2	1	0	-0.025	-0.096	0.050	0.057
Co ²⁺	4	2.426	1.301	1.039	0.086	0.119	0.048	0.347	0.354
Co ²⁺	0	1.478	1.429	0.027	0.021	0.606	0.535	0.310	0.317
Ni ²⁺	3	2.318	1.284	1.021	0.013	0.149	0.078	0.383	0.390
Ni ²⁺	1	1.365	1.286	0.068	0.011	0.625	0.554	0.383	0.390
Mg ²⁺	1	2.849	1.800	1.033	0.016	0.007	-0.064	0.136	0.143
Mo ⁶⁺	1	0.836	0.768	0.053	0.015	0.768	0.697	0.627	0.634
Mo ⁵⁺	2	1.039	0.901	0.123	0.015	0.699	0.628	0.564	0.571
Mo ⁵⁺	0	0.905	0.828	0.053	0.023	0.750	0.769	0.594	0.601
Mo ⁴⁺	3	1.046	0.903	0.123	0.020	0.687	0.616	0.561	0.568
Mo ⁴⁺	1	1.203	0.962	0.228	0.013	0.633	0.562	0.536	0.544

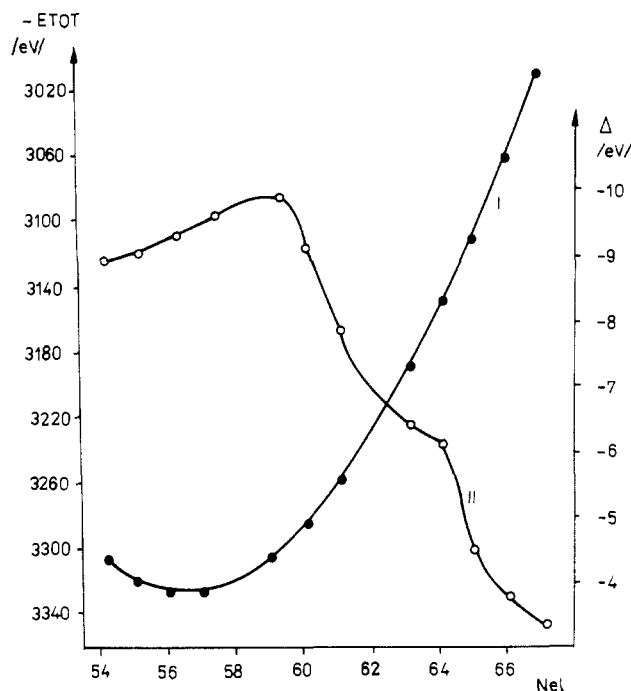


Figure 5. Total energy (curve I) and the difference of diatomic energy contributions $\Delta = E_{CH} - E_{OH}$ (curve II) as a function of the total number of electrons in the cobalt complex.

to 57. It is interesting that the total energy attains a minimum at the value of N_{el} smaller than 57. This indicates that lowering of the position of the Fermi level, i.e., by introduction of electron acceptor centers, would stabilize the complex. On the contrary, the energy of the reaction of hydrogen abstraction attains its maximum at N_{el} considerably higher than that of isolated complex. Thus it may be concluded that the activation of hydrocarbon molecule by Co-containing oxide catalyst should be favored by the introduction of small concentrations of electron-donor centers, whereas higher levels of doping would result in a strong decrease of the catalytic activity in this process.

The second step of the selective oxidation of propylene consists in a nucleophilic attack of an oxygen ion from the lattice of the catalyst on the allylic species. A model of the CoMoO₄ surface with adsorbed allyl is given in Figure 6. It is evident that the nucleophilic attack of the oxygen bonded to the molybdenum atom on the allylic species will be easier if a positive charge appears on the terminal carbon atoms in allyl. SCCC

Table II
Activity of the Isostructural Molybdates CoMoO₄, MnMoO₄, NiMoO₄, and MgMoO₄, and Their Related Oxides in Their Interaction with Propylene^a

catalyst	temp, °C	conversion of C ₃ H ₆ , %	selectivity, %			other products
			C ₃ H ₆ O	C ₃ H ₆	CO ₂	
CoMoO ₄	490	95	30	10	50	cracking
NiMoO ₄	490	22	81		19	
MnMoO ₄	490	30	36		39	cracking
MgMoO ₄	490	10			100	
CoO	450	95		30	20	cracking
MgO	490	4			100	

^a Pulse method: 1 pulse = 10.2×10^{-6} mol of C₃H₆.

MO quantum chemical calculation of the charge distribution, electronic configuration, and orbital energies of π -allyl complexes of Co, Ni, Fe, Mo, and Mg formed as intermediates were carried out.¹² The metal ions were assumed to be octahedrally coordinated by five identical oxygen ligands, the sixth ligand being allyl radical. Table I summarizes the results. In the case of complexes with Co²⁺ and Ni²⁺ ions, a considerable shift of π -allyl electrons to d orbitals of the metal takes place. It is interesting that in low-spin complexes the positive charge is mainly concentrated on the terminal carbon atoms in allyl. This may facilitate the nucleophilic attack of the lattice oxygen ion, resulting in the formation of an oxygenated complex as the precursor of acrolein. In the case of Mg²⁺ complex the allyl remains practically neutral, indicating a very weak bonding. The results of pulse reactor measurements of the activity and selectivity of these compounds are given in Table II.¹³ As seen from this table, CoMoO₄ and NiMoO₄ have a high activity and a good selectivity in the oxidation of propylene whereas MgMoO₄ is almost completely inactive. It seems that in the case of neutral allyl a situation is more conducive for dimerization.

Comparison of the theoretical and experimental results leads to the conclusion that ability of the cation to bind π -allyl is a condition necessary for its role as the active center in the first step of the oxidation of hydrocarbon. The nucleophilic attack of lattice oxygen on the allyl species leads in the subsequent step to the

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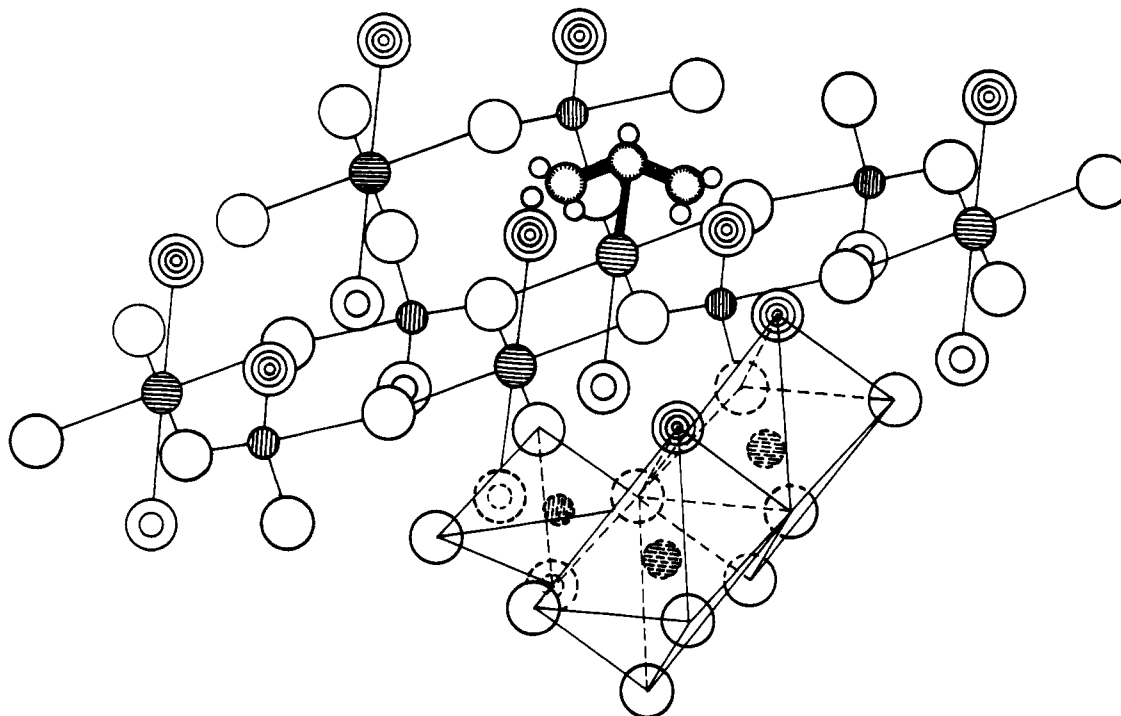
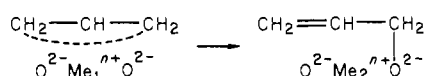


Figure 6. Model of the CoMoO_4 001 surface with adsorbed allyl species. \odot Mo; \ominus Co; \circ —oxygen in the 001 plane; \odot , \odot oxygen above and below the plane, respectively.

formation of a new intermediate complex of the ether character.^{14,15}



Complexes of this type were detected by using IR spectra¹⁶ during studies of the oxidation of propylene on the molybdates catalysts. In order for the reaction to continue, such complex must dissociate with desorption of the oxygenated organic molecule. This desorption is connected with removing of oxygen atom from the lattice. Many experimental results clearly indicate that this reaction is catalyzed by group 5, 6, and 7 metal oxides.¹⁷

We now consider our earlier question of which properties of these oxides are responsible for high activity and selectivity in the insertion of oxygen. One of the features common to all group 5, 6, and 7 metal oxide lattices known to be good catalysts for selective oxidation of hydrocarbon is their ability to form shear structures, related to the facility of the rearrangement of the mode, in which the coordination polyhedra are linked together. A hypothesis¹⁸ was advanced that the easy evolution of one oxygen ion on the transformation from corner-linked to edge-linked arrangement of metal-oxygen octahedra may be one of the factors which allow these structures to insert oxygen into organic molecules. The desorption is accompanied by the simultaneous rearrangement of octahedra which is known to proceed readily. This is at variance with other oxides, where the desorption of an oxygenated product

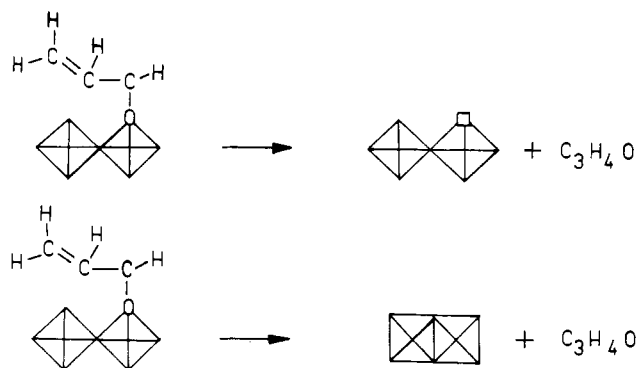


Figure 7. Mechanism of the insertion of oxygen into a hydrocarbon molecule.

must result in the generation of an oxygen vacancy and requires considerable expenditure of energy. The mechanism of the insertion is given in Figure 7.^{19,20}

Energies of the two transformations, shown in Figure 7, have been calculated using the SCF $X\alpha$ method²¹ for a model composed of two $\text{Mo}-\text{O}$ octahedra, corner linked (case a) and edge linked (case b). Results indicate that the energy of the system in case b is considerably lower than in case a, making route b much more favorable.

Let us now pass to the discussion of the mechanism of the third step of partial oxidation, consisting of the oxidation of the aldehyde to the acid. Comparison of the literature and patent data shows that on some catalysts such as bismuth molybdate or tin antimonate only acrolein is formed as the result of the oxidation of propylene, whereas with other catalysts, e.g., cobalt and nickel molybdates, acrolein and acrylic acid are ob-

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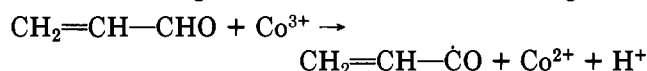
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tained in different proportions depending on the conditions of experiment. Thus, it may be concluded that a special type of active centers must be present at the surface of the catalyst, which has the ability to transform the aldehyde group into the carboxylic group irrespective of the type of organic molecule.

It is well-known that cobalt compounds are very effective catalysts in both homogeneous and heterogeneous oxidation of aldehydes to acids. In homogeneous reactions complexes of Co^{3+} ions with oxygenated organic ligands are used as catalysts; these involve Co ions surrounded by an octahedron of oxygen atoms. It has been postulated²² that the role of the Co^{3+} complex consists in the generation of radicals according to



These radicals react with oxygen to give the peracid radicals, which transform into peracid molecules. Acceleration of their decomposition is the second function of Co complexes. In the heterogeneous oxidation of acrolein, carried out at higher temperature, cobalt molybdate has been found to be an active and selective catalyst. Similarly as homogeneous catalysts it contains cobalt ions directly linked to oxygen ions in an octahedral arrangement. Many experimental data seem to indicate that in the step acrolein \rightarrow acrylic acid on cobalt molybdate catalysts it is the surface cobalt ion which is involved as active center. The molecular mechanism of the catalytic action of cobalt ions thus must account for the possibility of both processes, depending on the properties of the coordination sphere of cobalt ions, i.e., as either the isolated complex or the "complex" consisting of an element of crystal lattice.

The information on the type of bonding of acrolein in the intermediate complex may be obtained from infrared spectra of acrolein adsorbed at the surface of cobalt molybdate.²³ By using of this spectra a model of the surface intermediate complex has been formulated. This model was taken as the basis for quantum chemical calculations of the electron distribution and energy, carried out by the SINDO method.²⁴ Analysis of the results leads to the conclusion that a strong interaction exists between hydrogen atom of the aldehyde group and the nearest oxygen atom of the complex, resulting in considerable weakening of the CH bond. Thus a transformation may occur consisting of the transfer of a proton to oxygen with the heterolytic rupture of bond between the vinyl group and the Co ion. Such a transformation is equivalent to the initiation of the catalytic homogeneous oxidation. Our results indicate that there is a strong interaction of the planar oxygen of the complex not only with hydrogen but also with carbon of the aldehyde group, resulting in simultaneous weakening of the Co-O bond, as indicated in Figure 8. At elevated temperature of the heterogeneous process a concerted reaction may now occur, consisting of the transfer of proton from carbon to oxygen, formation of the bond between oxygen and carbon, and rupture of the Co-O bond, provided the lattice oxygen of the catalyst is mobile enough. Such concerted reactions may be considered as equivalent to

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Table III
Advantages and Limitations of Various Quantum-Chemical Methods

	ab initio SCF	EHT	CNDO(/2)	MINDO(/2)	X_α	SINDO
empirical parameters	no	ionization potentials, prop. factor in res. int.	ionization potentials, charge distributions	ionization potentials, bond energies, geometry	prop. factor in exchange potentials, ionic radii	ionization potentials, bond energies, geometry
electron distribution	good	exaggerated with good tendency	good	satisfactory or poor (dependent on version)	difficult to estimate	exaggerated with good tendency
changes of total energy	satisfactory	no possibility	exaggerated	usually good	no possibility by standard program	usually satisfactory, sometimes exaggerated
conformational analysis (geometry)	often poor	sometimes satisfactory, often poor	usually satisfactory, occasionally poor	usually satisfactory	no possibility by standard program	not analyzed so far
electron spectroscopy (UV-vis)	usually good	poor	very poor	poor	satisfactory (without term splitting)	satisfactory
photoelectron spectroscopy (PES)	often poor	poor	often satisfactory (UES)	poor	good	poor for small molecules, satisfactory for transition metal complexes (UES)
computer time required	often satisfactory, sometimes poor (XES and UES) very long	short	short	short	long	short

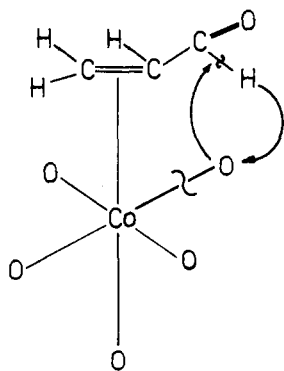


Figure 8. Concerted mechanism of the oxidation of acrolein to acrylic acid on a cobalt complex.

the insertion of oxygen into the C-H bond of the aldehyde group.

Conclusion

Results presented in this account show that the quantum-chemical description of intermediate complexes formed in the course of the catalytic reactions may supply valuable information concerning catalysis.

We have found modification of the reactivity of different bonds of the reacting molecule as the result of its interaction with the active center of the catalyst. This may contribute to an important degree to the understanding of the mechanism of the catalytic reaction and to identification of factors influencing its selectivity.

At present, exact discussion of the interaction of an adsorbed molecule with the group of atoms of the solid forming the active center is not yet possible, and many approximations must be introduced. The model chosen and the quantum-chemical method used depends on the particular problem to be solved. Advantages and limitations of various quantum chemical methods usually used to solve catalytic problems are summarized in Table III.

It may be hoped that with the development of quantum chemistry on one hand, and with further improvement in the knowledge of the mechanism of elementary acts in catalysis on the other hand, it will become possible to give a full description of the interactions between the reacting molecules and the catalyst as a basis for the development of the theory of catalysis.

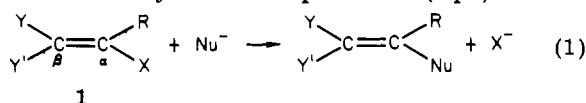
Nucleophilic Vinylic Substitution. A Single- or a Multi-Step Process?

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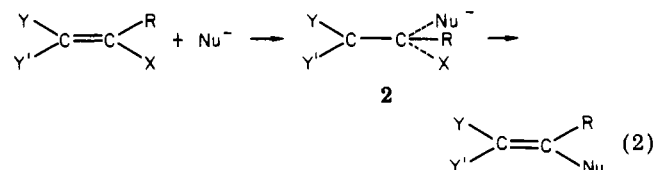
A vinylic system substituted by the leaving group X and the β -substituents Y and Y' (1) is an ambident electrophile, and many mechanistic routes are available for substitution by the nucleophile Nu⁻ (eq 1).¹ Two



routes, one involving nucleophilic attack on C _{α} ,¹⁻³ the other cleavage of the C-X bond to form a vinyl cation,⁴ are the formal analogues of familiar aliphatic substitution mechanisms. Others involve α,α , α,β , and α,β' elimination-addition routes via a carbene, an alkyne, or an allene, respectively,¹ radical routes via atom^{5a} or electron transfer,^{5b} initial prototropy or two S_N2' routes,¹ electrophilic addition-elimination,^{5c} and initial attack on X.^{5d} Most of these routes have been previously reviewed.¹⁻⁴

The purpose of this Account is to discuss a question common to substitutions at many unsaturated centers. Is the bimolecular substitution which involves nucleophilic

philic attack on C _{α} a single- or a multi-step process? The terms "addition-elimination" for the multi-step route,¹ "synchronous addition-elimination"⁶ for the concerted process, and "direct substitution"² have been used. I will use the descriptive terms "single-step process" when 2 (eq 2) is only a transition state and



"multi-step process" when 2 is an intermediate. Since some facts are apparently contradictory, opinions on this question have been divided in recent years.^{1-3,6,7} I will first present the evidence adduced in support of

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