Common Features of Photochemical, Radical, and Catalyzed Reactions

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Similarities between catalyzed reactions and the reactions of radical ions and electronically excited states derived from the parent compounds are pointed out. These similarities are illustrated by the *cis–trans* isomerization of 2-butene, the dimerization of ethylene, and the monomolecular decomposition of nitrous oxide. The results of this work should contribute to both the rationalization of the selection of a catalyst for the most varied reactions and the interpretation of catalyzed processes.

If one wished to perform a certain chemical conversion which under "standard" laboratory conditions (temperature of the laboratory, pressure about 1 atm, and/or in dilute solution) does not proceed spontaneously at a sufficient velocity, one would try to influence the reaction by thermal initiation. In some cases this leads to the desired effect; in most cases this means that the orbital as well as the spin parts of the wave functions of the reactants and the products (of the activated complex) are correlated (*1, 2*).

For many processes, however, the condition of orbital correlation is not fulfilled; some of them are, moreover, spin forbidden. However, one could still carry out these reactions by means of agents, whose action is reversible, which do not change the linking of the atoms in the studied molecule but which change the symmetry of the frontier orbital, as well as the multiplicity of the state. In this way the principal hindrance to the thermal initiation is suppressed, and the reaction frequently occurs. Examples of such agents are photons, electrons, protons, or electronically excited atoms. Similar results may be encountered with the use of an external electric or magnetic field.

The most significant products of these agents are radical ions (cations and anions) and electronically excited states, which often exhibit the character of biradicals. The influencing of the reactivity of molecules in this way has long been a tradition in chemistry, particularly in radical and photochemical reactions. Considerable attention has recently been paid to these two classes of reactions as well as to the electronic structure of radical ions (*3, 4*) and to electronically excited states (*5, 6*).

It is well known that overcoming of the above-discussed reaction path hindrances is also the subject of the entire field of catalysis where electron transfer plays an important role, too. Interaction between a reactant and a catalyst can be described as follows. Let us ascribe n molecular orbitals χ_i to the reactant R [m of them

belong to the symmetry type A, $(n - m)$ to the symmetry type B]. Let us further ascribe k molecular orbitals φ_i to the catalyst [t of them belong to the type A, $(k - t)$ to the type B]. Within the framework of the LCAO approximation the MO's of the reactant–catalyst complex (which we shall simply now term the "complex") are of the following form:

$$\Psi_j{}^A = \sum_{i=1}^{m} c_{ij}\chi_i{}^A + \sum_{i=m+1}^{m+t} c_{ij}\varphi_{i-m}{}^A,$$

$$\Psi_j{}^B = \sum_{i=m+t+1}^{n+t} c_{ij}\chi_{i-t}{}^B$$

$$+ \sum_{i=n+t+1}^{k+n} c_{ij}\varphi_{i-n}{}^B. \quad (1)$$

The summation

$$\sum_{j}^{occ.MO} (c_{pj})^2$$

can be interpreted as the electron fraction transferred from the catalyst into the p-th MO of the reactant (originally unoccupied).

Completely analogously an electron density loss from an originally doubly occupied MO of the reactant can be defined, e.g., as

$$[2 - \sum_{j}^{occ.MO} (c_{rj})^2].$$

Energy which is due to the interaction between catalyst and reactant molecule as well as the expansion coefficient values, c_{ij}, depend on the overlap and the energy difference of the interacting orbitals (7). Within the framework of the frontier orbital theory (8) all original molecular orbitals of the reactant (χ_i) and of the catalyst (φ_i) remain, in the first approximation, unchanged except frontier orbitals which form new MO of the complex:

$$\Psi_1{}^A = c_1{}^A\chi^A + c_2{}^A\varphi^A,$$
$$\Psi_2{}^B = c_1{}^B\varphi^B + c_2{}^B\chi^B, \quad (2)$$
$$\Psi_3{}^A = c_1{}^A\varphi^A - c_2{}^A\chi^A,$$
$$\Psi_4{}^B = c_1{}^B\chi^B - c_2{}^B\varphi^B.$$

$(c_2{}^A)^2$ represents the extent of electron

TABLE 1

Survey of Studied Types of Reactions: Parallelism between Noncatalytic and
Heterogenous Catalytic Reactions

Formation of	Reactions	
	Noncatalytic	Catalytic (11)
Radical cation	1. Action of oxidants (e.g., Lewis acid)	1. Semiconductor of the p-type: depletive chemisorption
	2. Electrooxidation	2. Semiconductor of the n-type: cumulative chemisorption
	3. Electron impact	
Radical anion	1. Action of reducing agents (e.g., alkali metals)	1. Semiconductor of the n-type: depletive chemisorption
	2. Electroreduction	2. Semiconductor of the p-type: cumulative chemisorption
	3. Absorption of thermal electrons	
Electronically excited state	Interaction with particles rich in energy: photons, electrons, electronically excited atoms (photosensitization)	Interaction of the reacting substance with transition element involving "backdonation" (12–14)

transfer from the reactant (χ^A) to the catalyst (φ^A) and $(c_2{}^B)^2$ may be taken as the extent of electron transfer from the catalyst (φ^B) to the reactant (χ^B). The value of the difference $(c_2{}^A)^2 - (c_2{}^B)^2$ means the charge localized on the reactant. In one extreme case when $c_1{}^A \cong c_2{}^A$ and $c_1{}^B \cong 1$, $c_2{}^B \cong 0$, the charge transfer is rather one-directional and the reactant molecule part of the complex approaches the radical cation. In another extreme case $c_1{}^B \cong c_2{}^B$; $c_1{}^A \cong 1$, $c_2{}^A \cong 0$, the radical anion is formed. Finally in the case of $c_2{}^A \cong c_2{}^B$, the situation of the reactant molecule part of the complex resembles, to a certain extent, the electronically excited state. Clearly enough, in real cases a whole spectrum of intermediate arrangements can exist. Because of the arguments[1] just presented it can be said that the reactant resembles, to a certain extent, the radical ions or electronically excited states; cf. Ref. (10). Therefore, it seems reasonable to *utilize recent experience from the above-mentioned spheres to study catalytic processes.* Table 1 presents a survey of the types of processes under consideration in this paper: the examples mentioned concern heterogenous catalysis; the extension to homogeneous catalysis could be done.

Another possibility exists for the role of a catalyst. This is a weak interaction between the reactant and the catalyst which leads to the formation of a van der Waals complex. Let us consider two cases of these complexes: (i) The case where charge transfer does not take place to a significant extent. Here the catalyst may act on the reactant to perturb the strict spin forbiddenness of the transition between the states of the reactant molecule

[1] After having finished the manuscript we obtained a reprint of a paper where the fate of ethanol, its radical ions and excited states are discussed under catalytic conditions (9).
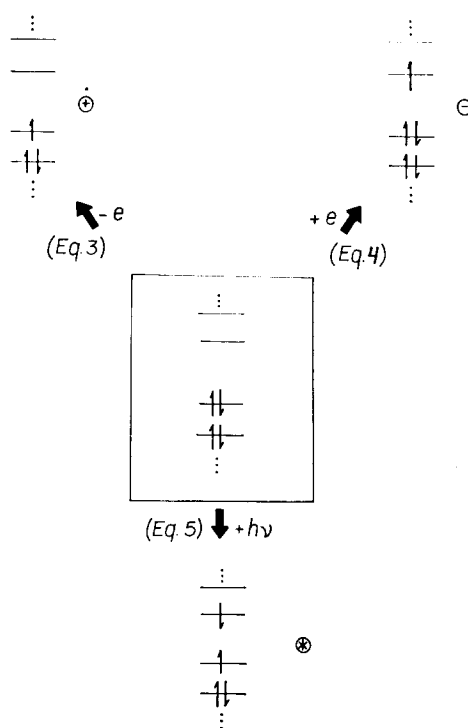

FIG. 1. Electron configuration of the initial system A, of the system after ionization ($\oplus$), after acceptance of an electron ($\ominus$), and after electronic excitation (*).

of different multiplicity. In this case, two mechanisms may become effective (15), one of which is based on the influence of a paramagnetic catalyst and the other one on the heavy atom effect (perturbation of the spin quantization due to spin–orbit coupling). The formation of a state of another multiplicity may also be realized by a mere electrostatic interaction between the reactant molecule and the charge of the catalyst surface. This usually leads to the removal of the degeneracy of the incompletely occupied orbitals of the reactant molecule. (ii) The case where charge transfer takes place. In neutral closed-shell systems this process leads to the formation of a structure which resembles a radical cation or a radical anion (see below).

TABLE 2

Properties of a Radical Cation, a Radical Anion, and an Electronically Excited State
in Relation to a Singlet Ground State (cf. Fig. 1)

| Radical cation ($\overset{\cdot}{\oplus}$)	Electronically excited state ("N → V₁")	Radical anion ($\overset{\cdot}{\ominus}$)
High electron affinity (easy reducibility)	High electron affinity (easy reducibility)	—
—	Low ionization potential (easy oxidizability)	Low ionization potential (easy oxidizability)
	Occurrence of an electronic transition in the low energy region (about 1 eV)[a]	
	Numerous transitions in visible or even in the near IR region	
	Weakening of "bond strength" in the system	
Extension of some bonds[b]	Extension of most bonds	Extension of some bonds[b]
Large increase of reactivity towards nucleophilic agents	Large increase of reactivity towards electrophilic and nucleophilic agents	Large increase of reactivity towards electrophilic agents
Paramagnetism	In case of T state paramagnetism	Paramagnetism
Change in symmetry of the state	Change in symmetry of the state	Change in symmetry of the state
Change in multiplicity	In case of T state change in multiplicity	Change in multiplicity

[a] In the theory of frontier orbitals, a necessary condition for easy monomolecular decomposition (2).

[b] Different bonds in the anion and the cation are as a rule extended.

In this connection the influence of the external (electric, magnetic) force field of a catalyst should be mentioned. This effect has already been discussed (16) in terms of a periodic force field. We shall discuss the influence of the external electric field in a separate communication.

CHANGES ACCOMPANYING IONIZATION, ACCEPTANCE OF AN ELECTRON AND ELECTRONIC EXCITATION

Figure 1 depicts schematically, in simplest MO terms, the formation of a radical cation (ionization), a radical anion (acceptance of an electron), and an excited state (N → V₁ excitation) from the system A:

$$A \rightleftarrows A^{\oplus} + e, \qquad (3)$$

$$A + e \rightleftarrows A^{\ominus}, \qquad (4)$$

$$A + h\nu \rightleftarrows A^*. \qquad (5)$$
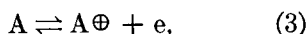
The orbital energy levels given in Fig. 1 show the reasons for the similarity between radical ions and excited states. The characteristic features of these systems are summarized in Table 2.

The remarkable increases of reactivity which often accompany the transition of the parent closed-shell system to radical ions, excited states, or to associates (complexes) with the catalyst, can be semiquantitatively interpreted by means of perturbation theory already adequately described by Bader (17) and Pearson (2). For our purposes only the second order term in the perturbation expansion of energy is critical:

$$q^2 \sum_{k=1}^{n} [\langle \Psi_0 | \partial U / \partial q | \Psi_k \rangle]^2 / (E_0 - E_k)$$

(q is a small shift along the reaction co-

ordinate, U is the operator of the potential energy, Ψ_i and E_i are eigenfunctions and eigenvalues of the original system (reactant molecule). If the absolute value of this term is to be relatively high, which corresponds to low activation energy of the reaction under study, the difference $E_0 - E_k$ must be small, and there must exist at least one low-lying excited state of the same symmetry as the ground state. It must be borne in mind that all modifications of the parent system discussed in this paper lead to systems characterized by a relatively high number of low-lying or even very low-lying excited states. This is a common feature of radical ions, excited states, and thus also of complexes between reactants and catalysts. All evidence accumulated in this section suggests that the state of the reactant molecule in the association with a catalyst can be frequently described, in the first approximation, by the radical cation, radical anion or excited state of the reactant
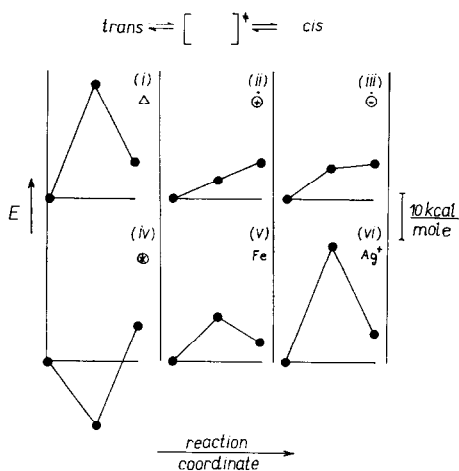

FIG. 3. Geometry of a model describing the catalysis by a Fe atom in *cis–trans* isomerization.

molecule. We demonstrate the applicability of this approach in the next section of this paper. Its use in the case of the catalytic decomposition of cyclopropane (*18*) and catalytic formation of ethylene oxide will be treated in another paper (*19*).

APPLICATION

1. cis–trans Isomerization of 2-Butene

The *cis–trans* isomerization of 2-butene is accompanied by a side reaction in which the double bond migrates (*20, 21*) to give 1-butene. In the activated complex we assume for the model reaction of the *cis–trans* isomerization that the p_z orbitals of the sp^2 hybridized carbon atoms lie in mutually vertical planes.

Figure 2 presents the results of the calculations of the total EHT energy for the *cis-* and the *trans-*isomer as well as for the activated complex. The considered model of the interaction of the 2-butene and the metal atom is obvious from Fig. 3. In Fig. 2 course (i) corresponds to the thermally initiated reaction; in courses (ii) and (iii), the reactant is the radical ion, and in course (iv), the reactant is the electronically excited state $(N \rightarrow V_1$; excitation from the 12th MO to the 13th MO); course (v) belongs to the reaction catalyzed by the Fe atom.[2] Its catalytic

FIG. 2. EHT energy of *cis-* and *trans-*2-butene, as well as of the corresponding activated complex: thermal initiation (i), radical cation (ii), radical anion (iii), $N \rightarrow V_1$ excited state (iv), influence of Fe (v), influence of Ag^+ (vi). In the cases (v) and (vi), the isomerization was carried out in the complex, in which the distance between the metal atom and butene was optimized.
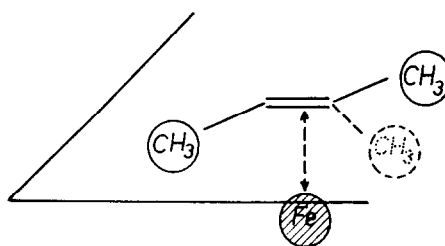
[2] The replacement of the surface of the metal by a single atom represents a very rough approximation. Nevertheless, it appears that even this simple

effect is due to the formation of the π-complex Fe-butene, in which a back-donation takes place. This complex is characterized by a simultaneous transfer of the electron density from the π-MO of butene into the d_{z^2} AO of iron and the transfer of the electron density from the d_{xz} AO of iron into the π*-MO of butene. In the complex with Fe these transfers result in an electronic state of butene which qualitatively resembles the first electronic excited state of butene. With the Ag+ ion [course (vi)] an effect similar to that of Fe is not encountered, because its atomic d orbitals are completely occupied. The results obtained are characteristic of numerous further processes. The transition from the parent substances to the radical ions results in an essential reduction of the activation energy; the transition to the excited state is even connected with the minimum on the curve of the potential energy, which belongs to the "vertical" arrangement. This corresponds experimentally as well as theoretically (23) to the proved vertical arrangement of the CH_2 groups in the first excited state of ethylene. The influence of the transition element does not manifest itself so distinctly as the $N \rightarrow V_1$ excitation, but only "catalytically," more specifically by a lowering of the barrier of the isomerization from 58 to 18.5 kcal/mol.

model can characterize to a certain extent the real behavior. This does not relate to sporadic cases; there exist experimental and theoretical evidence (22) elucidating this circumstance. It must be borne in mind, however, that an isolated atom represents only a part of the properties of a large group of atoms which is active on the surfaces of metals. In the case of the surface, there is generally greater probability of effective interaction with the reactant molecule due to the existence of the regions between neighboring atoms which have a different symmetry in relation to the reactant. The symmetric hindrances of interactions of the reactant molecule with the surface of the metal catalyst are therefore smaller than in the case of an isolated atom.

Clearly catalysts of another type could act as electron donors or acceptors; then the models including either the theoretical approach of a radical anion or a radical cation is pertinent.

Now let us also consider the migration of the double bond, for which a mechanism (20, 21) is considered which consists of two steps. The first step of the reaction, homolytic cleavage of the carbon–hydrogen bond (caused by the presence of the metal catalyst), has so far not been investigated quantum-chemically even on the qualitative level. If we consider that just this reaction plays a significant role in oxidation catalysis, it is appropriate to point out that the catalytic effect of the metal atom can be discussed in terms similar to that of the cis–trans isomerization. The interaction of the transition metal atom with the C–H bond (represented in Fig. 4) can obviously lead to the formation of a hydrogen atom and a methylallyl radical associated with the atom of the metal.
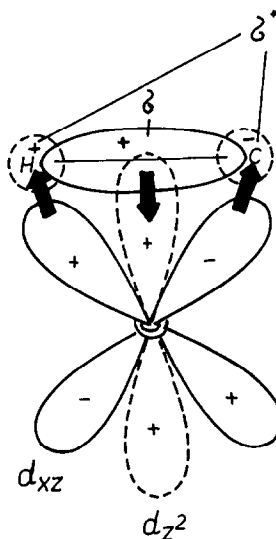

FIG. 4. Interaction of the molecular orbitals of the C–H bond with the atom of the transition element. The electron flow is indicated by arrows.

2. Cycloaddition of Ethylene, Leading to Cyclobutane

This reaction has been intensely studied by Woodward and Hoffmann (1) from the viewpoint of conservation of orbital symmetry. The process is a symmetry forbidden one in the ground state. It can be rendered allowable by electronic excitation in the photochemical sense (1) as well as catalytically (24, 25). The barrier corresponding to the thermally initiated process is also lowered if one of the reacting ethylene is converted into a radical ion: the reaction of the radical cation of ethylene with ethylene proceeds easily in the source of a mass spectrometer (26). The explanation of the facilitation of the course in terms of the Woodward-Hoffmann rules is obvious; in Fig. 5 we therefore limit ourselves to the qualitative elucidation based on the theory of frontier orbitals. It is appropriate to add that from the viewpoint of the law of conservation

TABLE 3

Wiberg's Bond Indices in N_2O, $N_2O^{\oplus}$, $N_2O^{\ominus}$, and N_2O^*

System	Bond	
	N–N	N–O
N_2O	2.34	1.49
$N_2O^{\oplus}$	2.17	1.62
$N_2O^{\ominus}$	1.87	1.20
N_2O^{*a}	1.53	1.54

[a] Nonlinear molecule: $\angle NNO = 134°$ (lowest excited singlet state).

of orbital symmetry, the barrier for radical ions is roughly halved as compared with that of neutral systems. Therefore, in the case of interaction between ethylene and a catalyst which is either a strong electron acceptor or donor the formation of the ethylene radical ions is to be expected. These radical ions, particularly the cation, tend to form a dimer with the neutral ethylene.

3. Decomposition of Nitrous Oxide

N_2O belongs to relatively stable oxides; its decomposition into N_2 and O only begins (27) at temperatures as high as 800–900°C: the dissociation of the N–O as well as the N–N bond occur in the ground state (thermal initiation).

It is possible to interpret the decomposition of the radical ions ($N_2O^{\oplus}$, $N_2O^{\ominus}$) and of the electronically excited states along similar lines as in the previous cases.[3] Exploiting the knowledge of the shapes of the frontier orbitals of N_2O (Fig. 6) and of the Wiberg bond indices (Table 3) it is possible, for example, to understand the fission of the N–N bond in the radical cation and of the N–O bond in the radical anion and the fission of both the N–N
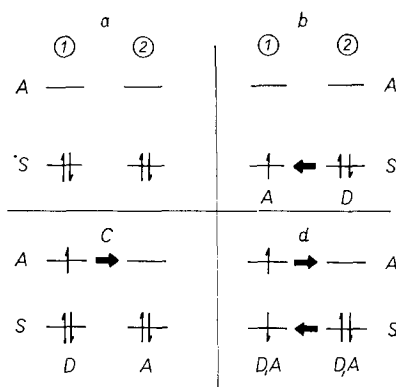
FIG. 5. Interaction between two ethylenes (1, 2) in different forms leading theoretically to different forms of cyclobutane from the viewpoint of the frontier orbital theory. (a) both molecules in the ground state, (b) one molecule converted to the radical cation, (c) one molecule converted to the radical anion, (d) one molecule in the electronically excited state. S and A denote symmetry of MO; the overlap between interacting MO is zero in case a, nonzero in the other cases. D and A denote donor and acceptor.

[3] A full discussion of this case including references may be obtained from the authors on request.
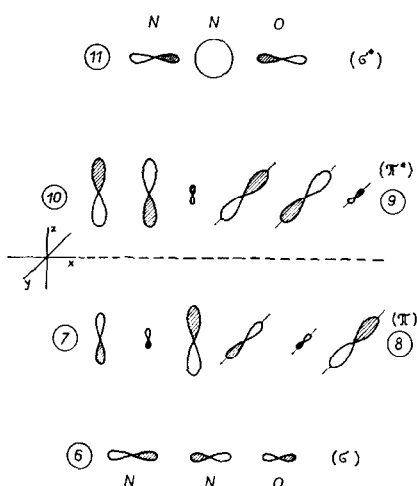
FIG. 6. Shape of the frontier molecular orbitals for N_2O.

and N–O bonds in excited states. Let us make just two more specific remarks. If the N–O bond is to dissociate preferentially, it is desirable to enrich the N_2O molecule by electrons. As sources of electrons it is possible to use successfully various catalysts: oxides which are semiconductors of the p-type [e.g., Cu_2O, NiO, CoO (*11*)], metals [Cu, Ag (*28, 29*)], as well as metal ions with an extremely low oxidation stage (*30*). In all cases N_2 and the oxygen anion are formed bound to the surface of the catalyst. If, on the other hand, the split of the N–N bond is to be favored, a catalyst has to be chosen which supports the radical cation formation. In the literature we have not found data on the catalytic decomposition of N_2O proceeding via $N_2O^{\oplus}$; it can be assumed, however, that N_2O on a catalyst with strong electron-acceptor properties would decompose into $NO^{\oplus}$ and N.

CONCLUSIONS

We believe that the approach described is particularly useful for analyzing processes in which a small molecule interacts with a catalyst. With many small mole-

cules energy gaps between orbitals are rather large and therefore the frontier orbitals play an important role. Indeed, with these systems experimental and theoretical experience suggests that the reactant molecule part of the reactant–catalyst complex and radical ions possess significant common features. The approach described can also be possibly applied to systems with a single double bond or with a few isolated or conjugated double bonds; in this case characteristic energy and space properties of π orbitals are relevant. With large σ-systems the situation is more complex.

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