

MO STUDY OF THE REACTIVITY OF CYCLOPROPANE, ITS RADICAL AND RADICAL IONS, AND MODELS OF ITS TRANSITION METAL COMPLEXES

S. BERAN and R. ZAHRADNÍK

*J. Heyrovský Institute of Physical Chemistry and Electrochemistry,
Czechoslovak Academy of Sciences, 121 38 Prague 2*

Received January 23rd, 1976

This paper is devoted to the quantum chemical (MINDO/2 and EHT) study of the reactivity of cyclopropane, its radical ions, cyclopropyl radical, and models of its surface complexes with iron. With all the cyclopropane forms noted, ring opening is the favoured type of decomposition on energy grounds. The MO data are used as the basis on which we discuss the mechanism of adsorption of cyclopropane on different transition metals and suggest the elucidation for their different catalytic activities.

The electronic structure of cyclopropane and its radical and ion forms has been studied in a series of theoretical papers. The similarity of the reactivity of cyclopropane systems to that of unsaturated compounds has been recognized. In numerous papers the presence of π -type molecular orbitals in cyclopropane has been reported¹⁻⁵. Buenker and Peyerimhoff⁶ counter, however, on the basis of *ab initio* calculations, that the unsaturated behaviour of cyclopropane is due rather to the σ MOs than due to the π MOs.

Elucidation of the reactivity of cyclopropane or its ion and radical forms is topical for the understanding of catalytic reactions of cyclopropane. From the viewpoint of the catalysis, cyclopropane is a very important system because it represents the simplest hydrocarbon which can be used for the study of both the activity and selectivity of catalysts. Recently several mechanisms were suggested for the adsorption of cyclopropane on metals: 1) formation of a π -complex with a metal surface⁷⁻¹⁰, 2) dissociative adsorption giving the cyclopropyl radical⁸⁻¹², 3) associative adsorption (accompanied with the ring opening^{9,10,13-16}), 4) simultaneous fission of two C—C bonds^{17,18}. Besides the mechanisms noted, a possible competitive process is the reaction of cyclopropane with hydrogen bound to the metal surface. Relevant also is the finding that the product of adsorption of cyclopropane on Pt and Pd is propane, whereas adsorption on Fe, Mo, Co, Ni, Ru leads to propane, methane and ethane⁹.

We think that the knowledge of the reactivity of cyclopropane systems and complexes of cyclopropane with metals may contribute to a better understanding of the interaction of cyclopropane with metal. For this reason we considered it expedient to undertake the MINDO/2 and EHT study of the reactivity of cyclopropane, its radical and radical ions, and model complexes of cyclopropane with transition metals. The results obtained are used for the MO interpretation of the mechanism of catalytic decomposition of cyclopropane on the transition metal surfaces. The catalytic processes are discussed along the same lines as in a previous paper¹⁹ *viz.* that the ground state of a substrate-catalyst complex is treated as a radical cation, radical anion or as an excited state, the choice of the model depending on the nature of the substrate and catalyst.

Methods

Open shell forms of cyclopropane were treated by the standard MINDO/2 method²⁰ combined with the open shell procedure of Longuet-Higgins and Pople²¹. This approach, examined by Čásky²², was incorporated into the procedure developed by Pancif²³ for geometry optimizations. This procedure reaches automatically for the minima on the energy hypersurface, *i.e.* it determines the geometries of stable structures. The course of the reaction is approximated by the passage between minima on the energy hypersurface over the saddle points by changing stepwise the length of a particular bond (or several selected bonds) and by optimizing automatically the geometry of the system after each step.

In our calculations the reaction path was identified with stretching of a particular C—C or C—H bond (or two selected bonds); the steps in stretching were 0.05 and $0.1 \cdot 10^{-10}$ m (description of the bond dissociation).

The calculations undertaken on the cyclopropane complexes with iron and platinum were of the EHT-type²⁴.

Up to now, EHT is the sole method capable of treating systems with heavy atoms at reasonable cost and for which sufficient experience has been accumulated. The diagonal $H_{\mu\mu}$ -elements were approximated either by setting them equal to the observed ionization potentials^{25,26} or by means of atomic orbital energies given by nonempirical SCF calculations²⁷. The first approach appears to give more realistic results. The off-diagonal $H_{\mu\nu}$ -elements were evaluated by means of the Wolfsberg-Helmholtz approximation²⁸. We take the EHT results with caution because of the known failures of the method. The most typical among them are overestimation of the ionic nature of the system (this depends on the input ionization potentials used), even qualitatively wrong predictions about the stability of complexes of organic compounds with metals, and considerable errors in estimated molecular geometries.

RESULTS AND DISCUSSION

In this section we have attempted to survey the theoretical and experimental data on the reactions of cyclopropane, their products and intermediates. The reactions studied are presented in Chart (p. 2308). Formally, they can be classified as follows.

A. *Uptake or loss of particles*: a) electron loss (reaction 1); b) electron uptake (reaction 2); c) loss of a hydrogen atom (reaction 3); d) uptake of a photon (reaction 4); e) perturbation by a catalyst (reaction 5).

B. *Bond fission in cyclopropane or in intermediates*: a) fission of C—C bonds: 1) one C—C bond; 2) two C—C bonds simultaneously); b) fission of C—H bonds.

The change in the bond strengths in cyclopropane upon an electron uptake, electron withdrawal, electron excitation, or H atom abstraction can be deduced from the shapes of the frontier orbitals of cyclopropane. In Fig. 1 we present the frontier orbitals of cyclopropane given by MINDO/2 and the Walsh orbitals. The MINDO/2 calculations for the optimal structure of the anion suggest the uptaken electron is housed in LUMO *b* which brings about weakening of a C—C bond and a minor decrease in the C—H bonding for H₃, H₄, H₅, and H₆ atoms (see Fig. 1 and Table I). Electron withdrawal from HOMO *a* weakens the C₇—C₉ and C₇—C₈ bonds and

TABLE I
Wiberg Bond Indices (for labelling of atoms see chart)

System	C_7-C_2 C_7-C_8	C_8-C_9	C_7-H_1	C_8-H_3
Cyclopropane ground state	0.97	0.97	0.97	0.97
Cyclopropyl radical	1.06	0.95	0.93	0.93
Carbene	1.04	0.98	—	0.95
Cyclopropane anion	0.98	0.57	0.95	0.86
Cyclopropane cation (form I)	0.64	1.08	0.97	0.96
Cyclopropane cation (form II)	0.73	0.57	0.95	0.97

strengthens the C_8-C_9 bonding. If an electron is removed from the HOMO *b*, all C—C bonds are weaker; the effect is most distinct on the C_8-C_9 bond.

Upon breaking down the C—H bond in cyclopropane, which gives rise to the cyclopropyl radical, the σ_{C-H} orbital is converted to a nonbonding MO. The latter is located on the C atom of the CH group and accommodates the unpaired electron. The C—C and C—H bond strengths are seen, from Table I, not to be affected considerably by this process.

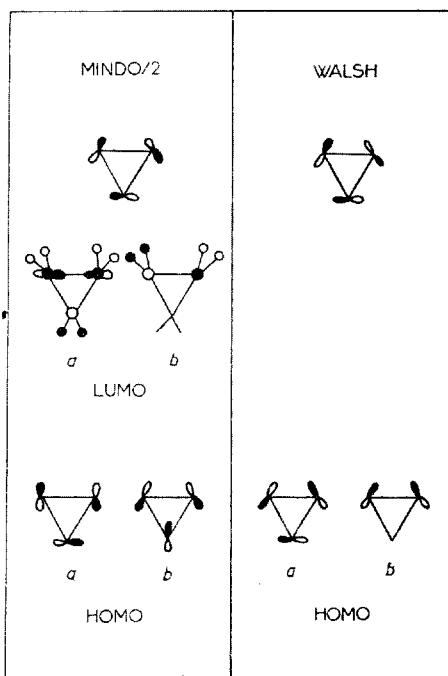
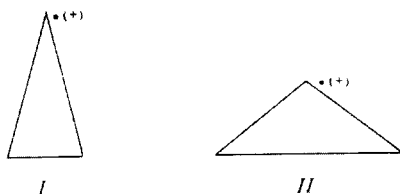


FIG. 1
MINDO/2 and Walsh Orbitals of Cyclopropane

Reaction of the cyclopropane cation. Enthalpy of reaction 1 is almost equal to the ionization potential of cyclopropane. MINDO/2 predicts the vertical and adiabatic ionization at 10.52 and 10.05 eV, respectively. Values of the observed ionization potential²⁹ range from 10 to 10.5 eV.

Our optimization procedure based on MINDO/2 gave for the structure of the cyclopropane radical cation almost the same result as the optimization reported by Haselbach³⁰ who made use of the simplex method.

From the two Jahn–Teller isomers (I, II) of cyclopropane the *I* form is 1.2 kJ/mol more stable than form *II*.



On the basis of Liehr's analysis and the calculations reported on the cyclopropenyl radical³¹, the *I* form appears to be the sole genuine minimum on the energy hypersurface. There are three minima of this type. A passage between them occurs *via* the flat form *II* (transition state) which is much lower in energy than the highly symmetrical C_{3v} form.

On stretching the C—C bond (reaction 1.1) in the cyclopropane radical cation to $2.7 \cdot 10^{-10}$ m, the MINDO/2 energy is 170 kJ/mol higher. This process brings about no significant changes in the other bond lengths; *e.g.* it is not accompanied

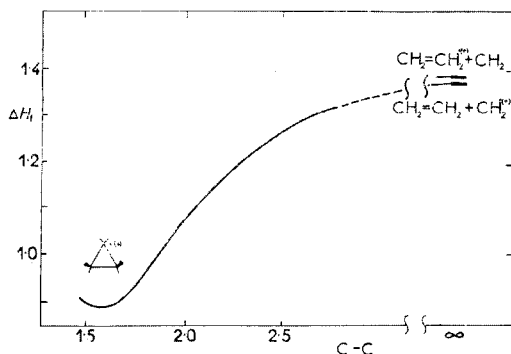


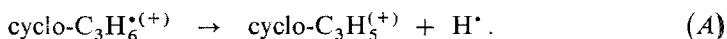
FIG. 2

Plot of the MINDO/2 Heats of Formation ΔH_f (in 10^{-3} kJ/mol) against the Lengths of C_7-C_8 and C_7-C_9 Bonds of the Cyclopropane Radical Cation (in 10^{10} m) (C_{2v} Splitting)

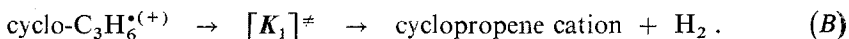
by the C—H bond fission. The energy curve is monotonous and exhibits no minimum which would correspond to a stable product of the trimethylene cation type.

Decomposition of the cyclopropane radical cation to $\text{CH}_2^{*\cdot(+)}$ and $\text{CH}_2=\text{CH}_2$ (reaction 1·2) is a symmetry-allowed process in contrast to the alternative decomposition giving $\text{CH}_2 + \text{CH}=\text{CH}^{*(+)}$ which is symmetry-forbidden (Fig. 2). The heats of reaction of the two processes are 473 and 485 kJ/mol.

Stretch of the C—H bond (reaction 1·3) to $2.0 \cdot 10^{-10}$ m while preserving the plane of symmetry is accompanied by a monotonous increase in energy. The energy of the system with the C—H bond length of $2.0 \cdot 10^{-10}$ m is higher than the sum of energies of isolated systems (cyclopropyl radical cation and H atom). It can be shown that the reaction (A) is symmetry-forbidden (curve 3, Fig. 3).



Ring opening of the cyclopropyl cation was examined by MINDO/2. The favoured mode of ring opening was found to be disrotatory with the energy of activation of 33 kJ/mol³²⁻³⁴. *Ab initio* calculations also favour the disrotatory opening and predict³⁵ the energy of activation of about 105 kJ/mol. If the C_{2v} symmetry is not maintained, however, the cyclopropane radical cation with the C—H bond stretched by $0.5 \cdot 10^{-10}$ m decomposes and the hydrogen molecule is expelled (curve 1, Fig. 3)



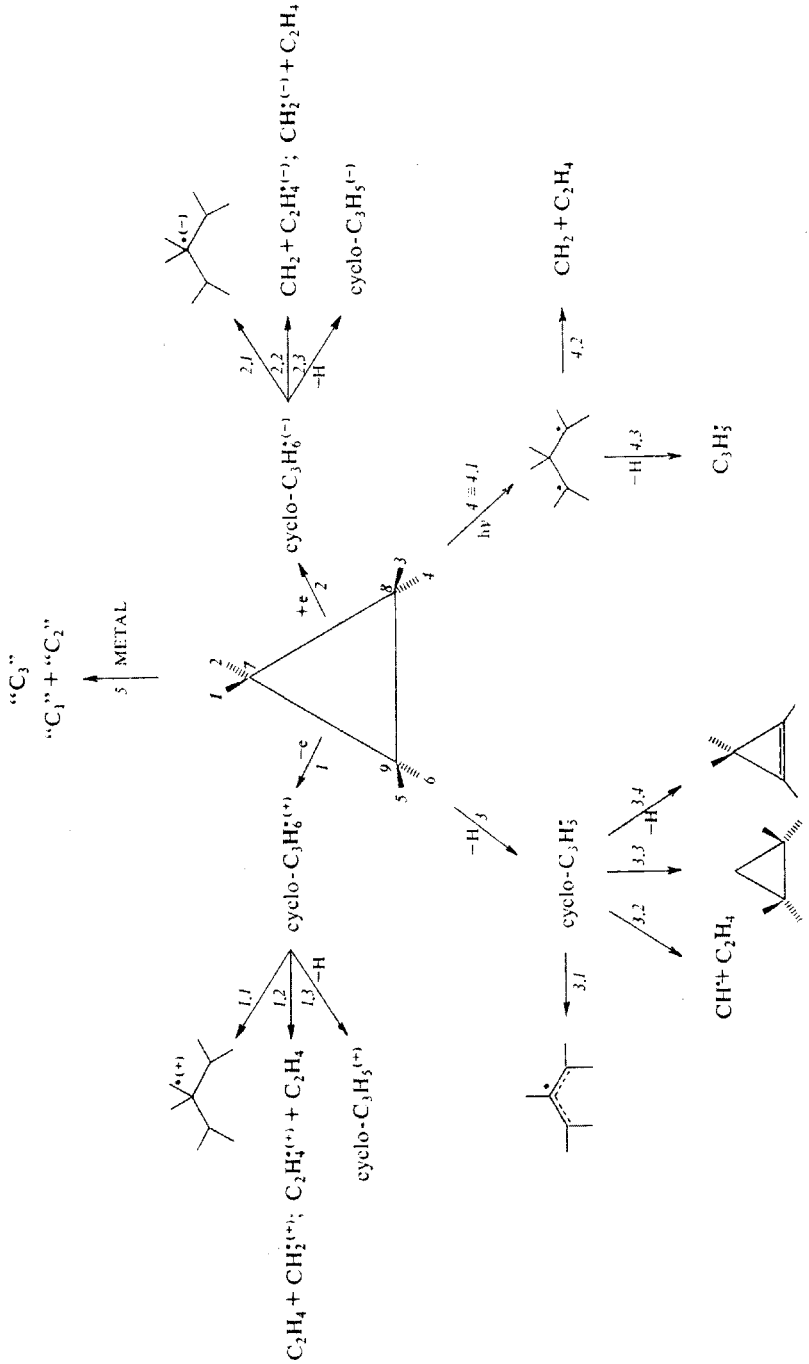
If the departure from the symmetry occurs at the C—H bond length of $1.8 \cdot 10^{-10}$ m, methylacetylene is formed (*cf.* curve 2 in Fig. 3)



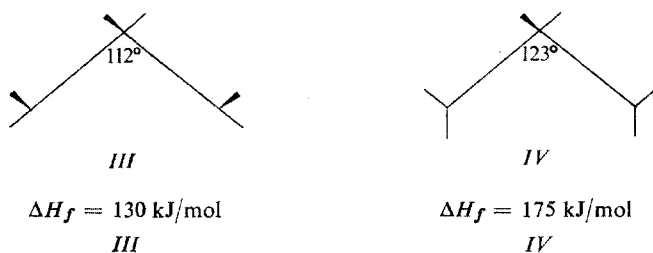
We have not yet succeeded in examining the activated complexes K_1^\ddagger and K_2^\ddagger because of the divergency of the variable metric method in critical regions.

Among reactions of the cyclopropane radical cation, MINDO/2 favours the process leading to cyclopropene cation and $\text{H}_2 \cdot$. Energetically somewhat less favourable is the reaction giving methylacetylene and $\text{H}_2^{*(+)}$ (Table II). The mere ring opening of the cyclopropane radical cation gives no stable products of the trimethylene type, but it requires only 170 kJ/mol. The process leading to the "C₁" and "C₂" fragments and the H atom abstraction requires much more energy.

Reaction of the cyclopropane radical anion. Reaction enthalpy of the addition of an electron to cyclopropane (electron affinity, reaction 2) is estimated by MINDO/2 to be 149 kJ/mol. This value corresponds to a vertical process, the estimated adiabatic electron affinity being 80 kJ/mol.



On stretching the C—C bond in the cyclopropane radical anion to $2.4 \cdot 10^{-10}$ m (reaction 2.1), the energy increases monotonously (Fig. 4). A small plateau on the potential curve at $2.4 \cdot 10^{-10}$ m corresponds most probably to the metastable trimethylene anion, whose terminal methylene groups are perpendicular to the CCC plane (form III). Passage to a stable form of the trimethylene anion (form IV) is associated with the barrier, which is due to the rotation of terminal methylene groups.



Decompositions of the cyclopropane radical anion leading to $\text{CH}_2^{\cdot(-)}$ and $\text{CH}_2=\text{CH}_2$ or CH_2 and $\text{CH}_2=\text{CH}_2^{\cdot(-)}$ (reaction 2.2) are symmetry-forbidden reactions. The expulsion of the methylene group from the cyclopropane radical anion was examined for the C—C bond lengths in the range from $1.5 \cdot 10^{-10}$ to $2.5 \cdot 10^{-10}$ m (Fig. 5). In this region we did not achieve energy barriers which would correspond to activated complexes of these symmetry-forbidden reactions. It is only possible to state that the SCF energy barrier is higher than 500 kJ/mol.

Dissociation of the C—H bond in the cyclopropane radical anion (reaction 2.3) is a symmetry-forbidden reaction, regardless of whether it leads to H or H^- . Exami-

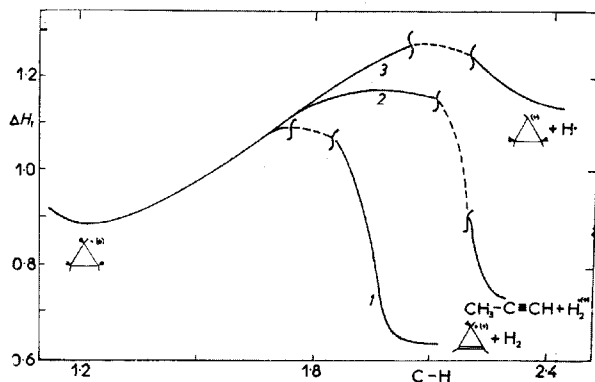


FIG. 3

Plot of the MINDO/2 Heats of Formation ΔH_f (in 10^{-3} kJ/mol) against the C-H Bond Length of the Cyclopropane Radical Cation (in 10^{10} m)

TABLE II

Heats of Reaction (ΔH_{298}^0) and Energy Barriers (ΔH_{298}^\ddagger) for Reactions of the Cyclopropane Radical Cation (kJ/mol)

Reaction	ΔH_{298}^0	ΔH_{298}^\ddagger	Products
1-1	—	—	^a
1-2	473	473	$\text{CH}_2^{*(+)} + \text{CH}_2=\text{CH}_2$
	485	\cong 485	$\text{CH}_2 + \text{CH}_2=\text{CH}_2^{*(+)}$
1-3	-251	209	cyclopropene cation + H_2
	-170	293	$\text{CH}\equiv\text{C}-\text{CH}_3 + \text{H}_2^{*(+)}$
	251	>377	cyclopropyl cation + H^\bullet

^a No stable product was found.

nation of this reaction by MINDO/2 showed that a stretch of the C—H bond by $0.3 \cdot 10^{-10}$ m brings about the change in symmetry of the wave function of the system. This manifests itself as a plateau on the energy curve (Fig. 5). The system of a changed symmetry is correlated now with the products of decomposition, cyclopropyl radical and the hydride anion (but not with cyclo- $\text{C}_3\text{H}_5^{*(-)}$ and H^\bullet). Continued stretching of the C—H bond $2 \cdot 10^{-10}$ m brings about a monotonous increase in energy but preserves the symmetry of the wave function. The heat of reaction of the cyclo-

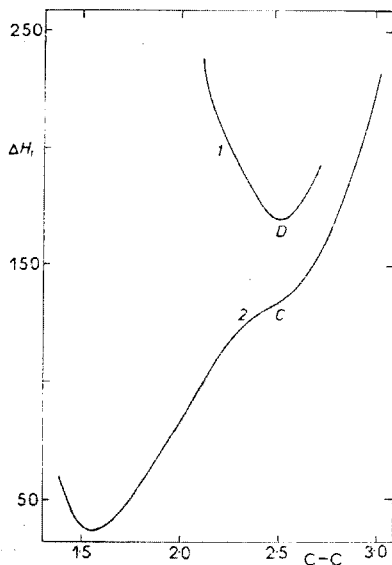


FIG. 4

Plot of the MINDO/2 Heats of Formation ΔH_f (in kJ/mol) against the C—C Bond Length of the Cyclopropane Radical Anion (in 10^{10} m)

1 Methylene groups in a planar configuration, 2 methylene groups are perpendicular to the plane of the ring; for III and IV see text.

TABLE III
Heats of Reaction (ΔH_{298}^0) and Energy Barriers (ΔH_{298}^\ddagger) of Reactions of the Cyclopropane Radical Anion (kJ/mol)

Reaction	ΔH_{298}^0	ΔH_{298}^\ddagger	Products
2·1	92	92	trimethylene anion ^a
	125	≥ 125	trimethylene anion ^b
2·2	335	>500	$\text{CH}_2^{\cdot(-)} + \text{CH}_2=\text{CH}_2$
	460	>500	$\text{CH}_2 + \text{CH}_2=\text{CH}_2^{\cdot(-)}$
2·3	222	222	cyclopropyl radical + H^-
	272	≥ 272	cyclopropyl anion + H^\bullet

^a Methylene groups are perpendicular to the CCC plane. ^b Planar trimethylene anion.

$-\text{C}_3\text{H}_6^{\cdot(-)} \rightarrow \text{cyclo-C}_3\text{H}_5^\bullet + \text{H}^-$ process is 222 kJ/mol, the heat of reaction of the $\text{cyclo-C}_3\text{H}_6^{\cdot(-)} \rightarrow \text{cyclo-C}_3\text{H}_5^{\cdot(-)} + \text{H}^\bullet$ process is 272 kJ/mol. For ring opening of the cyclopropyl anion, which gives allyl anion, the MINDO/2³²⁻³⁴ and *ab initio*³⁵ calculations favour the conrotatory mode. Its energies of activation estimated by the two MO approaches are 130 and 155 kJ/mol, respectively.

Ring opening of the cyclopropane radical anion is seen, from Table III, to be associated with the lowest energy barrier and the lowest heat of reaction among

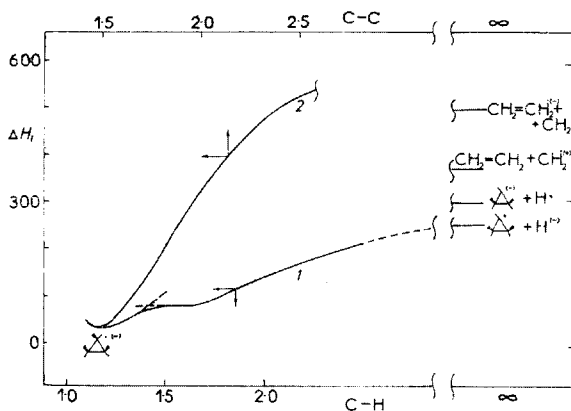


FIG. 5

MINDO/2 Heats of Formation ΔH_f (in kJ/mol)

1 Plot against the C—H bond length in the cyclopropane radical anion, 2 plot against the lengths of C_7-C_8 and C_7-C_9 bonds (C_{2v} splitting) in the cyclopropane radical anion (all bond lengths are in 10^{10} m).

TABLE IV

Heats of Reaction (ΔH_{298}^0) and Energy Barriers (ΔH_{298}^\ddagger) of Reactions of Cyclopropyl Radical (kJ/mol)

Reaction	ΔH_{298}^0	ΔH_{298}^\ddagger	Products
3·1	29	125 ^a	allyl radical
		226 ^b	allyl radical
3·2	512	512	$\text{CH}^\bullet + \text{CH}_2=\text{CH}_2$
3·3	430	430	cyclopropylidene + H^\bullet
3·4	272	≈ 272	cyclopropene + H^\bullet

^a Simple ring opening. ^b Mechanism involving hydrogen atom migration.

the reactions studied. Dissociation of the C—H bond and the reaction 3.2 appear to be the least feasible processes on energy grounds.

Reaction of the cyclopropyl radical. The heat of reaction estimated by MINDO/2 for the dissociation of the C—H bond in cyclopropane (reaction 3) is 285 kJ/mol.

Ring opening of the cyclopropyl radical (reaction 3·1) was the subject of both semiempirical (MINDO/2)^{32-34,36} and nonempirical studies³⁵. Both MO approaches suggested that the conversion of the cyclopropyl radical to the allyl radical is disrotatory. With our optimization procedure we arrived at the energy of activation of

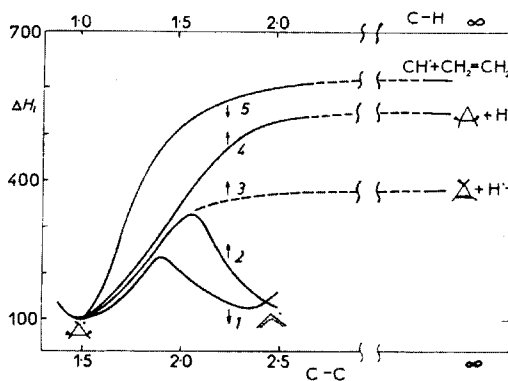


FIG. 6

MINDO/2 Heats of Formation ΔH_f (in kJ/mol)

1 Plot against the C-C bond length between the methylene carbons of the cyclopropyl radical; 2, 3 plot against the C-H bond length of the methylene group in cyclopropyl radical; 4 plot against the C-H bond length in the methine group of cyclopropyl radical; 5 plot against lengths of the C_7-C_8 and C_7-C_9 bonds (C_{2v} splitting) of cyclopropyl radical (all bond lengths are in 10^{10} m).

125 kJ/mol (Fig. 6), which was reported by Dewar and Kirchner previously³²⁻³⁴. The nonempirical calculation³⁵ gives the value of 335 kJ/mol.

Decomposition of the cyclopropyl radical to $\text{CH}_2=\text{CH}_2$ and CH^\cdot (reaction 3·2) is a symmetry-allowed process. The dissociation energy given by MINDO/2 is 512 kJ/mol (Fig. 6).

Reaction (3·3) is a symmetry-allowed process. The potential curve for the dissociation is smooth and the energy of dissociation is 430 kJ/mol. Bodor and collaborators³⁷ made use of MINDO/2 for the study of reactions of cyclopropylidene. Their estimates of the energy of activation is 57 kJ/mol for the formation of allene and 26 kJ/mol for the rearrangement to cyclopropene.

Fig. 6 presents an interesting course of the hydrogen atom abstraction from the methylene group of cyclo- $\text{C}_3\text{H}_5^\cdot$. After the initial stretch of the C—H bond of the methylene group, the hydrogen atom migrates to the methine carbon. This process is accompanied by simultaneous fission of the C—C bond which gives rise to the allyl radical. Hence, cyclopropene is not a product of the reaction because the rearrangement to the allyl radical is favoured on energy grounds. The energy of activation of reaction 3·4 is at least 272 kJ/mol.

Among the reactions of the cyclopropyl radical, the ring opening to allyl radical (Table IV) is the most likely one on energy grounds. Reaction 3·4, *i.e.* the C—H bond dissociation on the methylene carbon leading to cyclopropene, appears to be less likely. Energy requirements for the formation of "C₁" and "C₂" residues and carbene are even higher.

Photochemical Reactions*

The absorption spectrum of cyclopropane involves three regions of continuous absorption³⁸ in the vacuum ultraviolet region with the maxima at 120, 145, and 159 nm. Nonempirical calculations⁶ showed that the minima on the potential curves of the lowest triplet state and the first two excited singlet states correspond to structures with the CCC angle of about 120°. Thus excitation brings about ring opening. (Corresponding calculations were performed for the structure having methylene groups perpendicular to the CCC plane.) Sin and collaborators³⁹ arrived at similar results. According to their *ab initio* CI calculations for the lowest triplet state the methylene groups lie in the plane of the ring, the CCC angle is 110°, and the rotational barriers of the terminal methylene group are less than 4 kJ/mol. MINDO/2 calculations reported by Bodor and coworkers⁴⁰ as to the lowest excited state predict an open chain structure with the terminal methylene groups lying in the CCC plane.

* This section is based on the data taken from the cited papers. They are included here because we need them for the subsequent discussion.

Photolysis of cyclopropane⁴¹ at 147 nm gives rise to molecular and atomic hydrogen, methylene, allene, methylacetylene, and cyclopropyl radical.

It is seen from Table V that the C—C and C—H bond fissions in the excited cyclopropane are reactions with low energy barriers.

Model complexes of cyclopropane with Fe and Pt. The calculations undertaken on the interaction of the iron atom with cyclopropane were of the EHT type. The Fe atom was allowed to approach the centre of the ring or to the midpoint of a C—C bond in the plane of the ring or in the plane perpendicular to the latter. Experimental geometry of cyclopropane⁴² was used throughout. For all investigated modes of interaction we obtained potential curves with minima at the distance Fe — centre of the ring or Fe — midpoint of a bond of about $3 \cdot 10^{-10}$ m. Fig. 7 presents a particular case. If use is made of theoretical ionization potentials, the +2e charge is located on cyclopropane (in the optimum structure of the complex). On using experimental ionization potentials one arrives at uncharged cyclopropane. The latter case is more realistic since the formation of dinegative Fe anion in the former case is contrary to what is expected on chemical grounds.

Next calculations showed that the minima on potential curves do not correspond to stable complexes, because stretching of one, two, or three C—C bonds brings about decrease in energy of the complex. (From the literature⁴³ it is known that the stretch of the C—C bond in the isolated cyclopropane brings about an increase of the total EHT energy.) Our results suggest the interaction of cyclopropane with Fe atom does not result in any stable π -complex but rather it brings about ring opening of cyclopropane without any energy of activation. If the Fe atom approaches towards the apex of cyclopropane, the potential energy curve exhibits a distinct minimum, which is due to the interaction of the Fe atom with the C—H bonds of the methylene group. The calculations performed up to now suggest that the fission of the C—H bond of the methylene group is a process with an energy barrier. It thus appears that the formation of a stable complex iron-cyclopropyl (Fig. 8) is less probable than the ring opening of cyclopropane.

TABLE V

Heats of Reaction (ΔH_{298}^0) and Energy Barriers (ΔH_{298}^\ddagger) of Reactions of the Excited Cyclopropane⁴⁰ (kcal/mol)

Reaction	ΔH_{298}^0	ΔH_{298}^\ddagger	Products
4.1	0	0	trimethylene
4.2	220	228	$\text{CH}_2 + \text{CH}_2=\text{CH}_2$
4.3	215	—	cyclopropyl radical + H^\bullet

We also examined by EHT the interaction of cyclopropane with a Pt atom. A minimum on the potential energy curve was found at the distance Pt-cyclopropane of $5 \cdot 10^{-10}$ m. This conforms to what is known about EHT *viz.* that it gives unrealistic bond lengths for heavy atoms. For this reason no further calculations were attempted.

Model Interaction of Cyclopropane with the Metal Surface

We will discuss the interaction of cyclopropane with the metal surface in terms of frontier orbitals⁴⁴. The model of the interaction is presented in Fig. 9. We assume that close to the Fermi level there are surface states of electrons which may be taken as analogues of molecular frontier orbitals. Furthermore we adopt the following assumptions about the symmetry properties of these states: 1) Interactions between the HOMO of cyclopropane and unoccupied metal states and between the LUMO of cyclopropane and occupied metal states are symmetry allowed, 2) The total overlap in the two interactions considered in 1) is the same, 3) The total overlap is the same for all metals. The extent of the interaction (*i.e.* the degree of the electron transfer to the unoccupied state of metal or to the cyclopropane LUMO) is therefore given

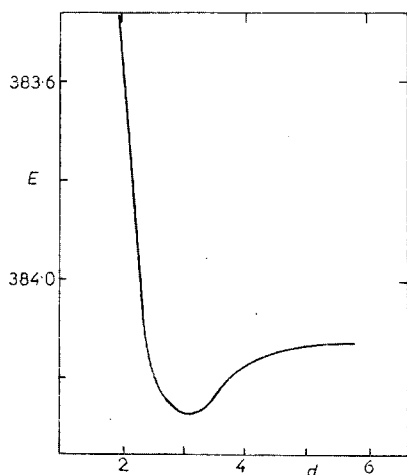


FIG. 7

Plot of the Total EHT Energy (in eV) against the Distance Fe—Centre of the Cyclopropane Ring d (in 10^{-10} m)

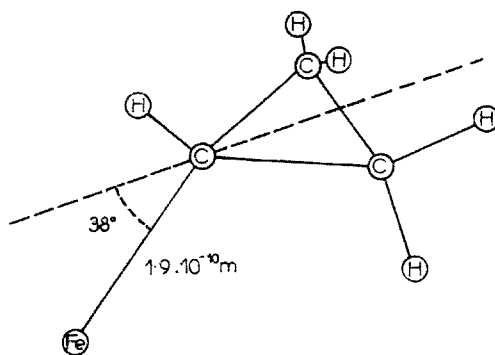


FIG. 8

Geometry of the Stable Cyclo- C_3H_5 -Fe Complex Given by EHT

In optimization of the Fe—C bond length, the Fe atom was maintained in the symmetry plane of cyclo- C_3H_5 , which passes through the methine carbon.

only by ΔE_1 and ΔE_2 (Fig. 9). According to the MINDO/2 calculations the midpoint between the HOMO and the LUMO of cyclopropane lies at -4.5 eV. Hence, if the energy of the Fermi level is of about -4.5 eV, then it holds that $\Delta E_1 \cong \Delta E_2$ and that the electron flow from the HOMO to the metal is roughly the same as the electron flow from the metal to the LUMO ($\delta_1 \cong \delta_2$). The net result of such an interaction is the transfer of an electron fraction δ_1 from the HOMO to the LUMO of cyclopropane. Another situation occurs with metals whose Fermi levels lie at lower energies than -4.5 eV. In such a case where $\Delta E_2 < \Delta E_1$ the interaction between the unoccupied states of metal and the HOMO of cyclopropane is more important than the interaction between the occupied states of the metal and the LUMO of cyclopropane. Hence it holds that $\delta_2 > \delta_1$. The lower is the energy of the Fermi level of the metal the higher is a positive charge of $\delta_2 - \delta_1$ located on cyclopropane. From the model presented it is possible to characterize the electronic structure of cyclopropane on the metal surface. If the Fermi level is of about -4.5 eV, it resembles the excited state. On metals with lower Fermi levels, it has features of the radical cation, whereas on metals with Fermi levels higher than -4.5 eV, it may be compared to the radical anion.

Notes on the Mechanism of Catalytic Decomposition of Cyclopropane on Transition Metal Surfaces

On energy grounds, the most probable reaction to occur for cyclopropane in the radical forms or in the excited state is ring opening (see Tables II – V). It is therefore

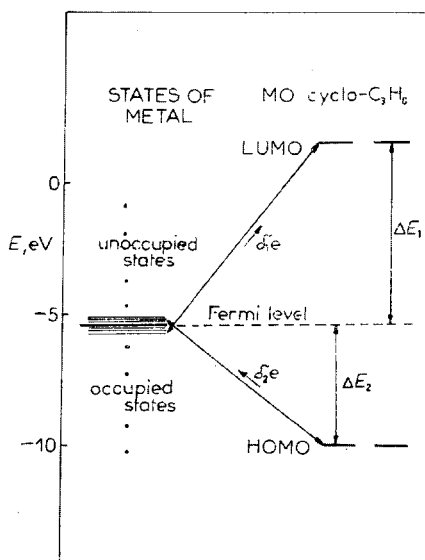


FIG. 9
Model of the Interaction of Cyclopropane with the Transition Metal Surface

possible to assume that the interaction of cyclopropane with the transition metal surface brings about ring opening provided *a*) the catalyst acts as an electron donor, *b*) the catalyst acts as an electron acceptor, *c*) the interaction cyclopropane-catalyst results in partial electron promotion in cyclopropane so that its electronic state resembles the excited state. We now comment in detail on the cases *b*) and *c*). If under the effect of a catalyst, the electronic structure of cyclopropane becomes similar to that of its radical cation, the least-energy reaction is simple ring opening which may eventually be accompanied by the expulsion of two hydrogen atoms. Consecutive decomposition to "C₁" and "C₂" fragments is a process with a rather high energy barrier. If the interaction gives rise to electronic excitation, ring opening occurs. The formed trimethylene may easily undergo two consecutive reactions: decomposition to "C₁" and "C₂" residues and C—H bond dissociation.

From the model assumed for the interaction it appears that the state of cyclopropane resembling its excited state is generated by metals with the Fermi level of about -4.5 eV. Hence, Fe, Co, Ni, and Mo bring about ring opening of cyclopropane and its consecutive cracking. On metals with the Fermi levels lower than -4.5 eV, a positive charge is accumulated on cyclopropane. The latter can approximately be taken as a radical cation and it is therefore possible to assume that the decomposition to "C₁" and "C₂" fragments is prohibitive on energy grounds. Experimentally⁹ it was found indeed that cracking of cyclopropane does not occur on metals with the work function higher than 5 eV (Pt, Pd). This accounts for the correlation^{4,5} suggested by Bastl, according to which the amount of cyclopropane cracking on the metal surface is inversely proportional to the Fermi level in absolute value.

Finally, on the basis of the quantum chemical calculations undertaken, we present several concluding remarks on the mechanisms proposed in the literature⁷⁻¹⁸ that were noted in the introduction: 1) Formation of a stable π -complex of cyclopropane with Fe appears to be improbable. Actually, the interaction of the cyclopropane ring with the Fe atom gives rise to a bond which may be taken as a π -bond, but the model calculations suggest that the interaction brings about decomposition of the ring. 2) Adsorption with a simultaneous cyclopropane ring opening is favoured over the dissociative adsorption. This follows from both the model calculations on the interaction of cyclopropane with the Fe atom and the considerations about the reactivity of perturbed forms of cyclopropane. 3) Adsorption accompanied by the cyclopropane ring opening appears to be the favoured reaction of cyclopropane with the metal surface. This mode of adsorption is predicted both by model calculations on the interaction of cyclopropane with the Fe-atom and the theoretical treatment of the reactivity of cyclopropane in perturbed forms. Nevertheless the calculations do not allow us to decide what are the optimal structures for the mono-, di-, and triadsorbed surface complexes of the open-chain form of cyclopropane. 4) This point concerns a simultaneous dissociation of the two C—C bonds in the ring, *i.e.* the fragmentation of the three-membered ring to "C₁" and "C₂" residues. By examina-

tion of the reactivity of perturbed forms of cyclopropane it appears that this process can hardly compete with ring opening.

We wish to express our thanks to Drs M. Černý, Z. Knor and Z. Bastl for drawing our attention and interest to the problem. Their comments on the manuscript and helpful criticism is gratefully acknowledged.

REFERENCES

1. Walsh A. D.: *Trans. Faraday Soc.* 45, 179 (1949).
2. Randić M., Maksić Z.: *Theor. Chim. Acta* 3, 59 (1965).
3. Bash H., Robin M. B., Kveben N. A.: *J. Chem. Phys.* 51, 52 (1969).
4. Merlet P., Peyerimhoff S. D., Buenker R. J., Shih S.: *J. Amer. Chem. Soc.* 96, 959 (1974).
5. Coffey P., Jung K.: *Theor. Chim. Acta* 34, 213 (1974).
6. Buenker R. J., Peyerimhoff S. D.: *J. Phys. Chem.* 73, 1299 (1969).
7. Bond G. C., Newham J.: *Trans. Faraday Soc.* 56, 1501 (1960).
8. McKee D. W.: *J. Chem. Phys.* 67, 1336 (1963).
9. Merta R., Ponec V.: 4th Internat. Congr. Catalysis, Paper No 50. Moscow 1968.
10. Anderson J. R., Avery N. R.: *J. Catal.* 8, 48 (1967).
11. Bond G. C., Turkevich J.: *Trans. Faraday Soc.* 50, 1335 (1954).
12. Addy J., Bond G. C.: *Trans. Faraday Soc.* 53, 383 (1957).
13. Addy J., Bond G. C.: *Trans. Faraday Soc.* 53, 368 (1958).
14. Roth J. A.: *J. Amer. Chem. Soc.* 92, 6658 (1970).
15. Merta R., Ponec V.: *J. Catal.* 17, 79 (1970).
16. Wallace H. F., Hayes K. E.: *J. Catal.* 29, 83 (1973).
17. Newham J.: *Chem. Rev.* 63, 123 (1963).
18. Beelen J. M., Ponec V., Sachtler W. M. H.: *J. Catal.* 28, 376 (1973).
19. Zahradník R., Beran S.: *J. Catal.*, in press.
20. Dewar M. J. S., Bodor N., Harget A., Haselbach E.: *J. Amer. Chem. Soc.* 92, 3854 (1970).
21. Longuet-Higgins H. C., Pople J. A.: *Proc. Phys. Soc., London* 68A, 591 (1955).
22. Čársky P., Zahradník R.: *Fortschr. Chem. Forsch.* 43, 1 (1973).
23. Pancíř J.: *Theor. Chim. Acta* 29, 21 (1973).
24. Hoffmann R.: *J. Chem. Phys.* 39, 1397 (1963).
25. Hinze J., Jaffé H. H.: *J. Chem. Phys.* 38, 1834 (1963).
26. Zerner M., Gouterman M.: *Theor. Chim. Acta* 4, 44 (1966).
27. Herman F., Skillman S.: *Atomic Structure*. Prentice-Hall Inc., Englewood Cliffs 1963.
28. Wolfsberg M., Helmholz L.: *J. Chem. Phys.* 20, 837 (1952).
29. Bodor N., Dewar M. J. S., Maksić Z. B.: *J. Chem. Phys.* 50, 654 (1969).
30. Haselbach E.: *Chem. Phys. Lett.* 7, 428 (1970).
31. Pancíř J., Zahradník R.: *Tetrahedron*, in press.
32. Dewar M. J. S., Kirchner S.: *J. Amer. Chem. Soc.* 93, 4290 (1971).
33. Dewar M. J. S., Kirchner S.: *J. Amer. Chem. Soc.* 93, 4291 (1971).
34. Dewar M. J. S., Kirchner S.: *J. Amer. Chem. Soc.* 93, 4292 (1971).
35. Farell L., Richards W. G.: *J. Chem. Soc. Chem. Commun.* 1973, 334.
36. Szeimies G., Boche G.: *Angew. Chem.* 83, 979 (1971).
37. Bodor N., Dewar M. J. S., Maksić Z. B.: *J. Amer. Chem. Soc.* 95, 5245 (1973).
38. Wagner P., Duncan A. B. F.: *J. Chem. Phys.* 21, 516 (1953).
39. Sin A. K. Q., John W. M. St., Hayes E. F.: *J. Amer. Chem. Soc.* 92, 7249 (1970).

40. Bodor N., Dewar M. J. S., Wasson J. S.: *J. Amer. Chem. Soc.* *94*, 9095 (1972).
41. Currie C. L., Okabe S. J. H., McNesby J. R.: *J. Phys. Chem.* *67*, 1494 (1963).
42. Sutton L. E.: *Tables of Interatomic Distances and Configuration in Molecules and Ions*. The Chemical Society, London 1958.
43. Hoffmann R.: *J. Amer. Chem. Soc.* *90*, 1475 (1968).
44. Fukui K.: *Fortschr. Chem. Forsch.* *15*, 1 (1970).
45. Bastl Z.: Private communication.

Translated by P. Čársky.