A QUANTUM CHEMICAL STUDY OF BUTENE REACTIONS ON MOLYBDATE CATALYSTS

Stanislav BERAN, Pavel JÍRŮ and Blanka WICHTERLOVÁ

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

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Both the EHT and IEHT methods were used in the study of interaction of various butene forms with models of catalytic active centers (Mo–O–metal), in which the Mo atom is in its +4 or +6 oxidation state and is tetrahedrally or octahedrally coordinated. The influence of an additional metal atom incorporated in the molybdate lattice was also studied. The results suggest that the interaction of all butene forms with the studied models of catalytic surface centers leads to the formation of stable adsorption complexes and that the butene molecule thus chemisorbed can undergo a direct *cis-trans* or a double-bond isomerization. It is shown that the probability of occurrence of both these reactions depends strongly on the symmetry of the surface center of the catalyst, on the valence of the Mo atom, and increases with the electron acceptor capability of the additional metal.

A number of authors have shown experimentally[2-7] that oxide catalysts are highly active in both the *cis-trans* and the double-bond isomerization of butenes. In the case of isomerization reactions on acidic oxide catalysts, the assumed intermediate product is 2-butylcarbonium ion, which is formed by addition of a proton to a butene molecule as a result of its interaction with the OH groups of the catalyst[3,4]:

$$\begin{tikzcd}
\text{1-butene} \arrow[r, shift left, harpoon] & \text{2-butylcarbonium ion} \arrow[l, shift left, harpoon] \arrow[r, shift left, harpoon] & \textit{cis}\text{-2-butene} \arrow[l, shift left, harpoon] \arrow[d, shift left] \\
 & & \textit{trans}\text{-2-butene} \arrow[u, shift left]
\end{tikzcd}$$

Another possible mechanism of isomerization of butene, taking place on basic oxide catalysts, is a reaction proceeding *via* a carbanion as intermediate product. This mechanism involves the dissociative adsorption of butene with a following stabilization of the proton formed by dissociation and of the formed *syn* or *anti* isomer of π-allyl anion on the O_2^- anion and metal cation, respectively[5-7]; it can be described by the following reaction scheme:

$$\begin{tikzcd}
 & & \text{1-butene} \arrow[dll, shift left] \arrow[drr, shift left] & & \\
\textit{cis}\text{-2-butene} \arrow[urr, shift left] \arrow[r, shift left, harpoon] & \textit{anti-}\pi \arrow[l, shift left, harpoon] \arrow[rr, shift left, harpoon] & & \textit{syn-}\pi \arrow[ll, shift left, harpoon] \arrow[r, shift left, harpoon] & \textit{trans}\text{-2-butene} \arrow[l, shift left, harpoon] \arrow[ull, shift left]
\end{tikzcd}$$

Both these mechanisms were studied theoretically with the aid of a model which involved the catalyst only implicitly as a donor or acceptor of an electron or proton[8,9].

The Mo–O–metal system is capable of catalyzing isomerizations, disproportionations, and various selective or total oxidations of unsaturated hydrocarbons. The reaction type depends on the oxidation state of Mo and its ligand field and on the electron acceptor or donor properties of the additional metal. Based on experimental data, the selective oxidation reactions are assumed to proceed *via* a π-allyl intermediate, the isomerization reactions *via* a carbocation, carbanion, or also a π-allyl complex[2].

In the present work, we attempted to study theoretically the possibility of a direct *cis-trans* isomerization of 2-butene (without dissociation of the original and formation of new bonds in the butene molecule) in its complexes with models of active centers of the Mo–O–metal catalyst. In addition, we followed also the possibility of dissociation of the C—H bonds in butene caused by its interaction with the catalyst, a first step of the double bond isomerization. The influence of the electron donor or acceptor properties and structure of the surface center of the catalyst on both reactions was also studied.

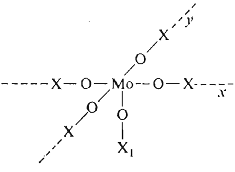
MODEL AND METHOD

In studying the solid phase or its interaction with molecules by the methods of quantum chemistry of molecules, it is inevitable to consider a limited number of atoms (cluster)[10] modelling this solid phase. The greatest problem is thentofinish this model so as to achieve the best agreement between its properties and the properties of a real crystal or catalytic center. The cluster is usually finished with hydrogen atoms[11] or pseudoatoms whose properties (parameters) are chosen so as to best represent the electron donor or acceptor properties of the remainder of the crystal[12].

The results of X-ray analyses suggest that the crystal lattice of MoO_3 or molybdates can be considered as an intermediate structure between the Oh and Td symmetries[13]; no information is obtained, however, about the structure of the catalytic surface centers. For this reason, the surface center of the catalyst was modelled by two types of clusters, *I* and *II*, corresponding to a cross section of an ideal crystallographic lattice of both limiting structures, octahedral and tetrahedral, and passing through the Mo atoms. The real catalyst surface is, however, besides Mo and O atoms and atoms of another transition metal, formed also by H atoms in the OH groups. Nevertheless, our models do not involve the surface OH groups or the O atoms projecting above the plane of the model, neither their interaction with butenes, since similar interactions were already theoretically studied[8].

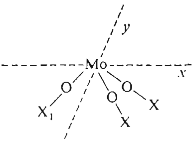
The lengths of the Mo—O and O—X bonds were $2 \cdot 10^{-10}$ m, which is approximately equal to the mean Mo—O bond length obtained experimentally for MoO_3 (ref.[13]). The Mo—O—X_1 bond is for the cluster *II* in the x—z plane. The cluster was terminated by means of pseudoatoms X on which a 5*s* Slater AO with the same exponent as 5*s* AO of Mo was localized. In order that this univalent pseudoatom exerted the same electron donor-acceptor properties as the modelled polyvalent transition metal atom, the H_{ii} element of the matrix **H** corresponding to this 5*s* AO was approximated by the valence orbital ionization potential (VOIP) for *d*-AO of the modelled metal (or by the identical dependence on the charge in the case of the IEHT (iterative extended Hückel theory) method). For all studied models of the catalytic surface centers and their interaction with the butene molecule, the formal oxidation state of the Mo atom was simulated by the total number of electrons involved in the calculation.

In studying the interaction of *trans*, *cis*, and the transition state (*) of butene with these clusters, the plane given by the double bond and C atom of the methyl group of butene was parallel to the *x*—*y* plane and the center of the double bond was placed above the Mo atom. The projection of the double bond into the *x*—*y* plane was at an angle of 0 or 45° with the *x* axis (for cluster I) and 0 or 90° for cluster II. The geometry of the individual butene structures[14] was in studying their interaction with the catalyst kept constant.



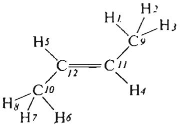
cluster *I*

C_{4v}

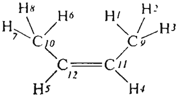


cluster *II*

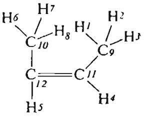
C_{4v}



trans-butene



cis-butene



transition state of butene (*)

The clusters modelling MoO_3 were calculated by the IEHT method with the use of the dependence of VOIP on *s*, *p*, and *d* electron densities[15]. Iterations were carried out only on the central atom and on pseudoatoms. The interaction of butenes with the models of surface centers of the catalyst was then studied with the use of the standard version of the EHT method[16]. The terms H_{ij} of the matrix **H** were in both methods expressed by the Wolfsberg–Helmholtz approximation[17] with the constant $K = 1{\cdot}75$. In the case of the Mo atom and pseudoatoms X, we used VOIP obtained by IEHT calculations for the corresponding clusters; these values for atomic orbitals *4d*, *5s*, and *5p* are about 15, 11, and 2 eV, respectively. The VOIP values for other atoms were taken from ref.[18]. Slater's exponents were obtained by the Burns' rules[19]. Mulliken's bond orders served to estimate the probability of dissociation of the C—H bonds of butenes in their adsorption complexes[20].

The influence of another atom which has weaker electron donor and stronger electron acceptor properties than the Mo atom and is built-in in the lattice (molybdate) was modelled so that the H_{ii} element corresponding to *5s* AO of an X_1 atom was set equal to 20 eV (in contrast to about 15 eV in the case of Mo). The influence of an atom with stronger electron donor and weaker electron acceptor properties than the Mo atom was simulated by VOIP equal to 7 eV.

RESULTS AND DISCUSSION

Adsorption

The potential curves for interaction of the double bond of *trans*, *cis*, and (*) butene with the mentioned models of the catalytic surface centers (six with C_{4v} symmetry and six with C_{3v} symmetry) were studied by the EHT method for both orientations of the butene molecule under consideration. The course of the calculated curves is identical for all the studied interactions and catalyst models; the EHT potential curves are smooth and monotonous in the range of distances from infinity to a minimum, and the minimum corresponds to a stable butene-catalyst adsorption complex (Fig. 1). The individual cases under study differ only by the position of the minimum (distance between the center of the double bond and the Mo atom) and by its depth (adsorption heat). From this point of view, the studied interactions can be divided into two significantly different groups: *a*) Interaction of butenes with an octahedral type of the catalytic surface center (cluster *I*), where for both studied modes of approach (0 and 45°) the equilibrium distance between the center of the double bond of butene and the Mo atom is about $3{\cdot}0 \,.\, 10^{-10}$ m (Fig. 1) and the adsorption heats of *trans*, *cis*, and (*) butenes are with small exceptions near 300, 300, and above 400 kJ/mol, respectively (Tables I and II). *b*) Interaction of butenes with a tetrahedral type of the catalytic surface center (cluster *II*) is stronger than the interaction with cluster *I*. The minimum on the adsorption curves is at the distance between the center of the double bond and Mo atom of about $1{\cdot}7 \,.\, 10^{-10}$ m (Fig. 1). The heats of adsorption given in Tables III and IV are all higher for cluster *I*. Both studied interactions of butenes with cluster *I* (0 and 45°) are for the same cluster type (the same $VOIP_{X1}$ and same oxidation state) from the energetic point of view practically identical (Fig. 1). The total EHT energies of the mutually corresponding adsorption complexes do not differ by more than 15 kJ/mol, except for the complex of *cis*-butene with the cluster Mo^{6+} ($VOIP_{X1} = 20$ eV), which is for the angle of 45° by 300 kJ/mol energetically more preferable than for 0°.

The situation is different in the case of interaction of butenes with cluster *II*, where the total EHT energy of the mutually corresponding adsorption complexes (hence also the adsorption heat) varies for both studied modes of approach (0 and 90°) much more significantly. The *trans* and *cis* isomers are more stable in the case of interaction where the projection of the double bond is at an angle of 90° with the x axis (Tables III and IV). Also the complex of (*) butene with the same cluster of Mo^{6+} ($VOIP_{X1} = 20$ eV) is for an angle of 90° about by 350 kJ/mol more stable than the same complex corresponding to an angle of 0°. In other studied cases, the complex of (*) butene for an angle of 0° is more stable, namely by up to 140 kJ/mol (Tables III and IV).

In the adsorption complexes of all studied butene structures and catalyst models, the double bond of butene is most affected in comparison with the electron structure of its ground state. In this case a pronounced forward donation of electrons from the π-MO of butene to the molecular orbitals of the cluster takes place in addition to a minor back donation of electrons from the cluster MO's to the butene π^*-MO (Fig. 2). Similarly, but less markedly, also other MO's of butene localized on its other bonds are perturbed. The perturbations of molecular orbitals localized on methyl groups of butene in its adsorption complexes (hence also weakening of the C—H bonds in these groups) are, however, stronger in the case of butene complexes

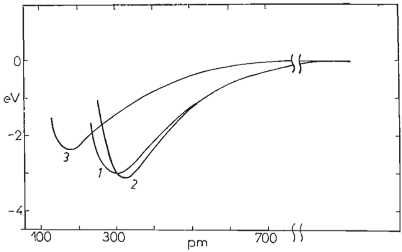


FIG. 1

EHT Potential Curves for Approaching of *trans*-2-Butene to MoO_3 Catalyst Model
1 Cluster *I*, Mo^{4+}, 0°; *2* Cluster *I*, Mo^{6+}, 0°; *3* Cluster *II*, Mo^{6+}, 0°.

TABLE I

Mulliken's Bond Orders of Butenes in their Complexes with Catalyst (Cluster *I*, 0°), *p*, Adsorption Heat ΔH (kJ/mol), Total EHT Energy of Each Structure (referred to energetically most stable arrangement) ΔE, and $\Delta E_{\text{cis-trans}}$ (kJ/mol) Obtained by EHT Method

Bond order	Mo^{6+}									Mo^{4+}								
	MoO_3			$VOIP_{X1} = 7$ eV			$VOIP_{X1} = 20$ eV			MoO_3			$VOIP_{X1} = 7$ eV			$VOIP_{X1} = 20$ eV		
	trans	*	*cis*	*trans*	*	*cis*	*trans*	*	*cis*	*trans*	*	*cis*	*trans*	*	*cis*	*trans*	*	*cis*
p_{1-9}	0·77	0·77	0·76	0·81	0·77	0·77	0·75	0·75	0·74	0·83	0·83	0·82	0·83	0·83	0·82	0·82	0·78	0·77
p_{2-9}	0·74	0·76	0·72	0·74	0·76	0·72	0·73	0·71	0·70	0·77	0·80	0·78	0·77	0·80	0·78	0·75	0·77	0·74
p_{3-9}	0·69	0·72	0·65	0·71	0·72	0·65	0·70	0·70	0·64	0·74	0·77	0·74	0·74	0·77	0·74	0·72	0·74	0·66
p_{4-11}	0·83	0·77	0·76	0·86	0·78	0·76	0·67	0·77	0·70	0·86	0·83	0·87	0·86	0·83	0·87	0·86	0·70	0·76
p_{5-12}	0·83	0·72	0·76	0·86	0·72	0·76	0·67	0·57	0·70	0·86	0·77	0·87	0·86	0·78	0·87	0·86	0·70	0·76
p_{6-10}	0·77	0·77	0·76	0·81	0·77	0·77	0·75	0·76	0·74	0·83	0·84	0·82	0·83	0·84	0·82	0·82	0·76	0·74
p_{7-10}	0·74	0·76	0·72	0·74	0·77	0·72	0·73	0·74	0·70	0·77	0·80	0·78	0·77	0·80	0·78	0·75	0·78	0·74
p_{8-10}	0·69	0·75	0·65	0·71	0·75	0·65	0·70	0·59	0·64	0·74	0·80	0·74	0·74	0·80	0·74	0·72	0·76	0·66
ΔH	311	441	333	305	438	320	272	359	334	288	436	267	296	447	277	269	440	287
ΔE	30	0	58	33	0	58	22	35	0	48	0	109	51	0	110	44	0	66
ΔE_{c-t}		—28			—25				22		—61			—59			—22	

TABLE II

Same as Table I, but for Cluster *I*, 45°

Bond order	Mo^{6+}									Mo^{4+}								
	MoO_3			$VOIP_{X1} = 7$ eV			$VOIP_{X1} = 20$ eV			MoO_3			$VOIP_{X1} = 7$ eV			$VOIP_{X1} = 20$ eV		
	trans	*	*cis*	*trans*	*	*cis*	*trans*	*	*cis*	*trans*	*	*cis*	*trans*	*	*cis*	*trams*	*	*cis*
p_{1-9}	0·83	0·79	0·65	0·84	0·79	0·65	0·56	0·76	0·63	0·85	0·85	0·84	0·86	0·85	0·84	0·78	0·79	0·66
p_{2-9}	0·74	0·76	0·77	0·75	0·76	0·77	0·72	0·71	0·74	0·77	0·80	0·77	0·77	0·80	0·78	0·73	0·77	0·77
p_{3-9}	0·67	0·68	0·67	0·67	0·68	0·67	0·62	0·66	0·65	0·70	0·73	0·71	0·70	0·73	0·71	0·67	0·70	0·70
p_{4-11}	0·84	0·77	0·78	0·85	0·77	0·76	0·60	0·74	0·70	0·85	0·82	0·86	0·86	0·83	0·86	0·69	0·78	0·76
p_{5-12}	0·84	0·72	0·76	0·85	0·72	0·76	0·60	0·64	0·70	0·85	0·77	0·86	0·86	0·77	0·86	0·69	0·72	0·76
p_{6-11}	0·83	0·74	0·65	0·84	0·77	0·65	0·56	0·63	0·63	0·85	0·84	0·84	0·86	0·84	0·84	0·78	0·76	0·66
p_{7-11}	0·74	0·79	0·77	0·75	0·75	0·77	0·72	0·74	0·74	0·77	0·79	0·77	0·77	0·79	0·78	0·73	0·75	0·77
p_{8-11}	0·67	0·76	0·67	0·67	0·79	0·67	0·62	0·78	0·65	0·70	0·82	0·71	0·70	0·82	0·71	0·67	0·79	0·70
ΔH	303	445	333	296	441	328	309	442	659	304	445	275	297	455	284	330	492	363
ΔE	42	0	52	45	0	53	310	343	0	41	0	110	58	0	111	62	0	69
ΔE_{c-t}		—10			—8			310			—69			—53			—7	

TABLE III

Same as Table I, but for Cluster *II*, 0°

Bond order	Mo^{6+}									Mo^{4+}								
	MoO_3			$VOIP_{X1}$ = 7 eV			$VOIP_{X1}$ = 20 eV			MoO_3			$VOIP_{X1}$ = 7 eV			$VOIP_{X1}$ = 20 eV		
	trans	*	*cis*	*trans*	*	*cis*	*trans*	*	*cis*	*trans*	*	*cis*	*trans*	*	*cis*	*trans*	*	*cis*
p_{1-9}	0·81	0·78	0·76	0·81	0·78	0·76	0·81	0·75	0·56	0·84	0·83	0·82	0·84	0·83	0·83	0·82	0·81	0·79
p_{2-9}	0·80	0·79	0·79	0·80	0·79	0·79	0·74	0·78	0·78	0·81	0·81	0·81	0·81	0·81	0·81	0·81	0·79	0·80
p_{3-9}	0·75	0·74	0·74	0·77	0·78	0·76	0·70	0·76	0·76	0·78	0·78	0·78	0·80	0·79	0·80	0·78	0·79	0·78
p_{4-11}	0·75	0·69	0·72	0·75	0·69	0·73	0·65	0·68	0·71	0·79	0·77	0·78	0·79	0·77	0·78	0·77	0·71	0·75
p_{5-12}	0·70	0·61	0·67	0·70	0·61	0·67	0·61	0·50	0·65	0·74	0·64	0·70	0·75	0·63	0·69	0·75	0·63	0·70
p_{6-10}	0·84	0·82	0·81	0·84	0·83	0·81	0·80	0·65	0·56	0·85	0·83	0·83	0·84	0·83	0·83	0·85	0·83	0·82
p_{7-10}	0·75	0·80	0·74	0·75	0·81	0·74	0·69	0·78	0·70	0·73	0·80	0·77	0·78	0·81	0·77	0·73	0·80	0·74
p_{8-10}	0·68	0·80	0·67	0·68	0·80	0·67	0·60	0·77	0·64	0·71	0·80	0·73	0·73	0·80	0·75	0·69	0·80	0·68
ΔH	258	640	316	272	667	341	341	641	459	217	773	308	204	724	272	372	741	420
ΔE	282	0	264	295	0	266	227	0	149	456	0	405	422	0	394	269	0	261
ΔE_{c-t}		18			29			78			51			28			8	

TABLE IV

Same as Table I, but for Cluster *II*, 90°

Bond order	Mo^{6+}									Mo^{4+}								
	MoO$_3$			VOIP$_{X1}$ = 7 eV			VOIP$_{X1}$ = 20 eV			MoO$_3$			VOIP$_{X1}$ = 7 eV			VOIP$_{X1}$ = 20 eV		
	trans	*	*cis*	*trans*	*	*cis*	*trans*	*	*cis*	*trans*	*	*cis*	*trans*	*	*cis*	*trans*	*	*cis*
p_{1-9}	0·82	0·83	0·64	0·84	0·83	0·64	0·81	0·83	0·64	0·84	0·84	0·84	0·85	0·85	0·84	0·84	0·85	0·67
p_{2-9}	0·78	0·79	0·75	0·79	0·79	0·76	0·78	0·79	0·75	0·80	0·80	0·79	0·80	0·80	0·79	0·80	0·80	0·77
p_{3-9}	0·74	0·76	0·75	0·74	0·77	0·75	0·72	0·74	0·72	0·76	0·78	0·76	0·77	0·78	0·76	0·76	0·78	0·76
p_{4-11}	0·71	0·69	0·66	0·74	0·68	0·66	0·59	0·60	0·66	0·78	0·84	0·78	0·79	0·79	0·79	0·78	0·68	0·65
p_{5-12}	0·72	0·48	0·60	0·72	0·49	0·66	0·72	0·44	0·66	0·78	0·61	0·78	0·77	0·61	0·79	0·75	0·54	0·68
p_{6-10}	0·81	0·77	0·64	0·81	0·78	0·64	0·77	0·73	0·64	0·84	0·83	0·84	0·84	0·80	0·84	0·82	0·81	0·67
p_{7-10}	0·72	0·78	0·75	0·72	0·79	0·76	0·69	0·75	0·75	0·80	0·82	0·79	0·80	0·82	0·79	0·73	0·80	0·77
p_{8-10}	0·53	0·79	0·75	0·53	0·79	0·75	0·52	0·70	0·72	0·66	0·79	0·76	0·66	0·80	0·76	0·55	0·79	0·76
ΔH	298	602	405	287	593	393	417	1 025	816	211	595	341	207	590	335	376	692	476
$\Delta E \Delta E$	204	0	137	206	0	140	508	0	149	284	0	194	283	0	195	216	0	156
ΔE_{c-t}		67			66			359			90			88			60	

with models represented by clusters *I* and *II*. This reflects the circumstance that an interaction of molecular orbitals localized on the methyl groups of butene with molecular orbitals localized on the O atoms whose distance from the H atoms of the CH_3 groups is $2 \,.\, 10^{-10}$ m takes place in the adsorption complexes of butene with cluster *I* as a result of more favourable geometrical factors. In this way it is also possible to explain the different equilibrium distances in adsorption complexes formed by cluster *I* or *II*. Transfers of electron densities between the butene molecule and the catalyst model cause the formation of a positive charge localized on the butene molecule interacting with the catalyst, however its pseudoexcitation takes place at the same time. The quantity of the electron density transferred between the molecular orbitals of the butene and catalyst depends on the electron donor or acceptor properties of the cluster and determines to a large extent the reaction properties of butenes adsorbed on the individual types of clusters. The magnitude of the positive charge localized on the butene molecule forming a complex with the catalyst shows for the studied interactions the following trend: Mo^{6+} ($VOIP_{X1} = 20$ eV) $<$ $<$ $Mo^{6+}(MoO_3) \approx Mo^{6+}$ ($VOIP_{X1} = 7$ eV) $\approx Mo^{4+}$ ($VOIP_{X1} = 20$ eV) $< Mo^{4+}$. .$(MoO_3) = Mo^{4+}$ ($VOIP_{X1} = 7$ eV).

cis-trans *Isomerization*

The reaction of *cis-trans* isomerization of butene is in the electron ground state of butene inhibited for symmetry and spin reasons. The activation barrier of this reaction calculated by the EHT method is 60 kJ/mol and the reaction enthalpy is 40 kJ/mol[21].

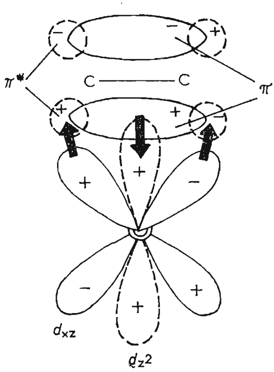


FIG. 2

Interaction of π-Molecular Orbital of Butene with Molecular Orbitals of the Catalyst Model

The flow of electron densities is denoted by arrows.

It is seen from Tables I and II and Fig. 3 that the order of stability of the adsorption complexes of the individual butene forms is for the model of the catalytic surface center, represented by cluster *I*, Mo^{6+} ($VOIP_{X1} = 20$ eV), for both interaction types (0 and 45°C) the following: *cis* > *trans* > (*). The values of the reaction enthalpy of *cis-trans* isomerization of butene (Tables I and II) adsorbed on this type of the catalyst center suggest that, in contrast to the gas phase reaction, the formation of the *cis* isomer is here preferred (Fig. 3). For other models of surface centers represented by cluster *I*, the order of stability of the butene adsorption complexes is as follows: (*) < *trans* < *cis* (Tables I and II). The energetic course of the *cis-trans* isomerization is qualitatively the same as that for the excited state of butene[21], *i.e.*, the activation barrier of this reaction is removed and the *trans* isomer is more stable than the *cis* isomer (Fig. 3). The reaction enthalpy of the *trans-cis* isomerization is for both types of butene adsorption complexes with cluster *I* (0 and 45°) and models Mo^{6+} (MoO_3), Mo^{6+}($VOIP_{X1} = 7$ eV), and Mo^{4+}($VOIP_{X1}$

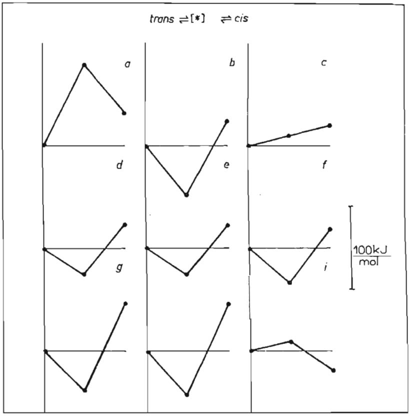


FIG. 3

EHT Energies for *cis*, *trans*, and the Transition State (*) of Butene

a) Thermal initiation, *b*) $\mathrm{N} \rightarrow \mathrm{V}_1$ excited state, *c*) radical cation; and their complexes with cluster *I*, 0° for models: *d*) Mo^{6+}, MoO_3, *e*) Mo^{6+}, $VOIP_{X1} = 20$ eV, *g*) Mo^{4+}, MoO_3, *h*) Mo^{4+}, $VOIP_{X1} = 7$ eV, *i*) Mo^{6+}, $VOIP_{X1} = 20$ eV.

= 20 eV) one half as large or lower than the reaction enthalpy of this reaction in the gas phase (Tables I and II). Hence, both the *cis* and *trans* isomers can be products of desorption in these cases, although the formation of the *trans* isomer is more probable for energetic reasons. For butene complexes with the models $Mo^{4+}(MoO_3)$ and $Mo^{4+}(VOIP_{X1} = 7\ eV)$, the reaction enthalpy of *cis-trans* isomerization is higher than the reaction enthalpy of this reaction in the gas phase. The probable desorption product is the *trans* isomer.

The stability of the adsorption complexes of the individual butene forms (0 and 90°) with the catalyst models represented by cluster *II* decreases in the order $(*) > cis > > trans$ for all studied models. The barrier for the *trans-cis* isomerization is again removed and the type of desorption products is determined by the isomerization reaction enthalpy (Fig. 4). It follows from the values in Tables III and IV that the product of interaction of butenes with catalyst surface center with a structure of the cluster *II* will be prevailingly *cis*-butene in all studied cases.

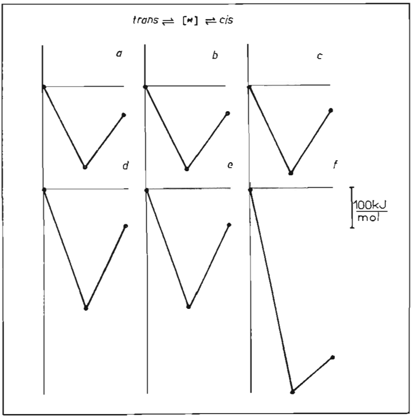


FIG. 4

EHT Energies for *cis*, *trans*, and (*) Butenes in their Complexes with Cluster *II*, 45°

a) Mo^{6+}, MoO_3, *b*) Mo^{6+}, $VOIP_{X1} = 7$ eV, *c*) Mo^{4+}, $VOIP_{X1} = 20$ eV, *d*) Mo^{4+}, MoO_3, *e*) Mo^{4+}, $VOIP_{X1} = 7$ eV, *f*) Mo^{6+}, $VOIP_{X1} = 20$ eV.

Isomerization of Double Bond

Our aim was to study the possibility of the double bond isomerization involving an allyl type particle as intermediate product. The first step of isomerization by this mechanism is splitting off of hydrogen from the methyl group of butene under formation of an adsorbed allyl particle.

The values of Mulliken orders of C—H bonds of butenes forming adsorption complexes with catalyst surface centers suggest that these bonds are more or less weakened in comparison with the bond orders of butene in the gas phase, where they are equal to 0·85. The degree of weakening of these bonds depends on the character of the catalyst center with which the butene interacts; it increases with the electron acceptor properties of the catalyst (Tables I – IV).

In complexes of the individual butene forms with cluster *I* (0 and 45°), the lowest bond orders are assigned to the H atoms of the methyl groups, H_3 and H_8, (hence also the highest dissociation capability), in rare cases also to the H_1 and H_6 atoms as can be seen from Tables I and II. These bonds are weaker for butene complexes with Mo^{6+} than with Mo^{4+}. The presence of a metal with stronger electron acceptor properties than Mo (model of catalyst with $VOIP_{X1} = 20$ eV) has also a positive influence on the probability of dissociation of the C—H bonds; their perturbation increases with electron acceptor properties of the transition metal X1 (with its VOIP value) (Tables I and II).

In complexes of *cis* and *trans*-butenes with catalyst models represented by cluster *II* (0 and 90°), similarly to the preceding case (with small exceptions), the C—H bonds corresponding to the H atoms of the methyl groups H_8 (eventually H_1, H_3, H_6) are most affected as can be seen from Tables III and IV. In complexes of (*) butene, however, the weakest C—H bonds correspond to the H_4 and H_5 atoms (Tables III and IV). In view of the fact that the existence of the adsorption complexes of (*) butene is for energetic reasons more probable than the existence of the *cis* and *trans* isomers (Tables III and IV, Fig. 4), we may assume that the dissociation of C—H bonds of the H_4 and H_5 atoms in butene complexes with surface centers of the cluster *II* type catalyst is more probable than for the H atoms of the methyl groups. This is probably caused by the character of the proposed model of the catalytic surface center, which does not involve the surface atoms directly interacting with molecular orbitals of butene localized on its methyl group. The catalyst models represented by cluster *II* correspond namely to the extreme case of a surface center in which the Mo atom emerges above the catalyst surface.

Interaction of butenes (0°) with clusters of a C_{3v} symmetry (modelling also the surface center Td MoO_3), where the pseudoatoms X and the Mo atom lie in a single plane (*i.e.*, in positions with a mirror symmetry with respect to the plane determined by the O atoms, as compared with cluster *II*) – cluster *IIb* – causes a more significant weakening of the C—H bond of the butene methyl groups as is apparent from the Mulliken bond orders (Table V).

Moreover, the stability order of the butene complexes with the catalyst models according to *trans* > *cis* > (*) (Table V) is quite different from the stability order in the case of their complexes with cluster *I* and *II* (Tables I–IV). The equilibrium bond length, the double bond center – Mo atom, is about $2 . 10^{-10}$ m for the complexes of the *trans* and *cis* isomer as compared with $3 . 10^{-10}$ m for the (*) butene complex.

It is hence apparent that the stability of the complexes of the individual butene forms and thus the character of the products of their reaction with the catalyst (Mo–O–metal) is significantly influenced by the geometry of the active centers of this catalyst. If we assume that the discussed case of a tetrahedral center corresponds to a plane of ideal, tetrahedrally arranged MoO_3, and the center represented by cluster *II* corresponds to a deffect of such an ideal surface (where the Mo atom projects above the surface plane), then the obtained results suggest that both the activity and selectivity of the catalyst are strongly influenced by the defects of its surface and their structure. It should be noted that a number of other (not discussed here) surface defects or structurally different active centers of the catalyst can be considered as well; and the stability of their complexes with the butene forms, hence also the products of the catalytic reaction, can be quite different.

TABLE V

Mulliken's Bond Orders of Butenes in their Complexes with Catalyst (Cluster *IIb*, 0°), *p*, Total EHT Energy of Each Structure (referred to energetically most stable arrangement) ΔE and $\Delta E_{cis-trans}$ (kJ/mol) Obtained by the EHT Method

Bond order	Mo^{6+}, MoO_3			Mo^{4+}, MoO_3		
	trans	*	*cis*	*trans*	*	*cis*
p_{1-9}	0·80	0·78	0·62	0·82	0·84	0·80
p_{2-9}	0·80	0·75	0·79	0·81	0·80	0·80
p_{3-9}	0·64	0·64	0·63	0·70	0·72	0·69
p_{4-11}	0·80	0·80	0·69	0·82	0·82	0·81
p_{5-11}	0·67	0·67	0·67	0·73	0·75	0·72
p_{6-12}	0·73	0·73	0·66	0·78	0·80	0·74
p_{7-12}	0·76	0·76	0·79	0·78	0·79	0·80
p_{8-12}	0·60	0·75	0·61	0·66	0·79	0·66
ΔE	0	92	43	0	79	43
$\Delta E_{cis-trans}$		43			43	

CONCLUSIONS

Our results suggest that the *cis-trans* isomerization of 2-butene can on the proposed models of the Mo–O–metal catalyst proceed directly by rotation of the methyl group by 180° around the double bond. The energetic barrier corresponding to this reaction in the ground state of 2-butene is removed for most of the proposed models of the catalyst surface centers owing to a transfer of electron densities between the π-molecular orbitals of butene and the molecular orbitals of the catalyst (pseudoexcitation). The reaction enthalpy of *trans-cis* isomerization of butene interacting with the catalyst and hence the equilibrium between the *trans* and *cis* isomers depends strongly on the structure of the surface center and its donor–acceptor properties (*i.e.*, on the oxidation state of Mo and electron donor–acceptor properties of an additional transition metal). It was also shown that the interaction of 2-butene with the active center of the catalyst can lead to the formation of an allyl particle as intermediate product of the double bond isomerization, especially on centers with an octahedral structure. Also this reaction depends strongly on the electron donor–acceptor properties of the surface centers and its probability increases with the electron acceptor properties of the additional transition metal.

Our MO studies revealed the significant role of the oxidation state of molybdenum, of the additional metal and its electron acceptor properties, and of the symmetry of the ligand field of the active center. The known experimental data about reactions on the Mo–O–metal catalysts substantiate the great role of the mentioned factors in changing the course of the catalytic reactions of unsaturated hydrocarbons with respect to different products[2,22–24]. However, in view of the fact that the sole symmetry of the ligand field of the active center influences appreciably its interaction with the olefine, it is very difficult to make general conclusions concerning a comparison of the bulk oxidation states, ligand field *etc.* of the catalyst with its activity and selectivity in conversions of unsaturated hydrocarbons without the knowledge of the actual surface states of the real Mo–O–metal catalyst surface.

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