

A Frontier Orbital Investigation of the Mechanism of Epoxidation of Alkenes Using $[\text{MO}(\text{O}_2)_2, \text{M}=\text{Cr}, \text{Mo}, \text{W}]$

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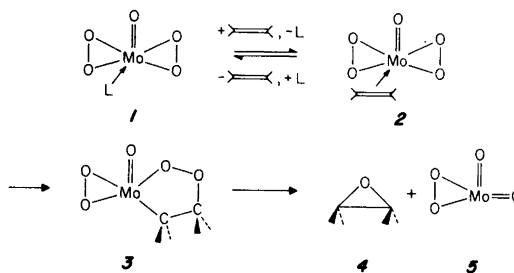
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The epoxidation of alkenes by η^2 -peroxo complexes of group VI transition metals was analyzed from a frontier orbital point of view. The orbitals of the η^2 -peroxo complex are constructed from transition metal oxide and peroxide fragments. The coordination of ligands and the preferred orientation of the alkene at the transition metal center was studied. Different slipping motions of the alkene towards the peroxo oxygen, as well as a 1,3-dipolar cycloreversion from a dioxometalocycle were analyzed. It is suggested that an important component of the reaction mechanism is a slipping motion of the transition metal-bound alkene in a perpendicular or parallel orientation (relative to the transition metal peroxo plane) towards one of the peroxo oxygens. This motion is controlled by a favourable interaction between the π^* orbital of the alkene and the lone pair on the oxygen which is antisymmetric with respect to the transition metal peroxo plane, or antisymmetric relative to the oxygen in the transition metal peroxo plane.

The epoxidation of alkenes is an important reaction from a synthetic and commercial point of view, and can be achieved by a variety of reagents.¹ In recent years, increased interest has been focused on transition metal-catalysed epoxidation, and a series of reviews² and books³ on this subject have been published. Among the reagents studied, especial attention has been devoted to the η^2 -peroxo complexes of the group VI transition metals (Cr, Mo, W; especially Mo), because these are highly effective for selective epoxidation of alkenes at room temperature in aprotic solvents. The reaction has been found to be stereoselective: *cis* alkenes give *cis* epoxides and *trans* alkenes give *trans* epoxides.⁴

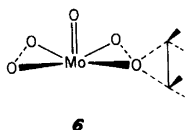
As to the mechanism, Mimoun *et al.*^{2,4} have advocated a five-membered dioxymetalocycle as the active intermediate, whereas Sharpless *et al.*⁵ have suggested reaction of the alkene with one of the peroxy oxygens. According to Mimoun^{2,4} and others,⁶ the first step is a reversible formation of an alkene transition metal complex, 2, in the rate



Scheme 1

determining step, followed by irreversible oxygen transfer to the alkene (Scheme 1). NMR spectroscopic investigations revealed that HMPA (L in Scheme 1) was displaced from the transition metal during the reaction, and addition of HMPA to the reaction mixture had a large inhibitory effect on the rate of epoxidation.^{2,4} Kinetic experiments also indicate a binding of the alkene to the metal center as the first step.⁶ As Mo(VI) has no *d* electrons available for back-bonding to the alkene, it is supposed that the alkene loses its nucleophilic nature upon coordination, making pos-

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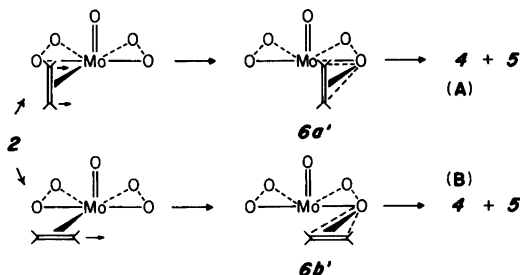


sible the nucleophilic attack of the coordinated oxygen via an intramolecular 1,3-dipolar cycloaddition giving 3.^{2,4} The resulting five-membered dioxometalloycle, 3, then decomposes by 1,3-dipolar cycloreversion to produce the epoxide, 4, and the molybdenum complex, 5. Intermediates such as 3 have been isolated from reactions of Pt⁷ and Rh⁸ peroxocomplexes with cyano-substituted alkenes.

The isolated dioxometalloycle is well supported in the group VIII cases, but Sharpless *et al.*⁹ have recently claimed that this mechanism is not operative with *d*⁰ early transition metals (group IV, V and VI). They have also demonstrated the peroxy origin of the transferred oxygen using ¹⁸O labeling studies and suggested a three-membered transition state, 6, (above) as the active intermediate. This mechanism is in accordance with Bartlett's widely accepted mechanism for the epoxidation of alkenes by peroxy acids,¹⁰ which has recently received theoretical support.¹¹

It is our intention here to present a theoretical investigation of this type of epoxidation reaction so as to throw some light on the mechanism and the intermediates involved. For this purpose, the frontier orbital approach and extended Hückel calculations^{12,13} have been used. In all the calculations we have utilized molybdenum as the transition metal.

We will in the following investigate two general forms of epoxidation mechanism (A) and (B). The first step in both mechanisms is a binding of the alkene to the molybdenum atom in MoO(O₂) giving 2. In mechanism (A) the next step is a slip-



ping of the alkene to a perpendicular position relative to the molybdenum peroxy plane giving a three-membered transition state, $6a'$, which is very similar to the intermediate suggested by Sharpless *et al.*⁵

The other mechanism, (B), is a parallel slipping motion of the alkene along the molybdenum peroxy bond giving the three-membered intermediate, $6b'$. The slipping motion here can be compared with the postulated transition metal activation of alkenes towards nucleophilic attack.¹⁴ The dioxometalloycle, 3, can to some extent be viewed as an intermediate in mechanism (B) and a 1,3 cycloreversion leading to 4 and 5 will also be examined. Another variant of mechanism (B) is a parallel slipping motion of the alkene along the molybdenum peroxy bond below the molybdenum peroxy plane.

Let us start with the frontier orbitals of MoO(O₂)₂, which can be considered as two peroxides bonded to a MoO fragment. The interaction diagram for this interaction is shown in Fig. 1.

The two peroxy orbitals with *p_x* character interact with the *xy* and *x²-y²* orbitals of molybdenum to give a planar MoO₄ unit perpendicular to the MoO axis. An angle of 45° is expected for the orientation of the dioxygen ligands, because

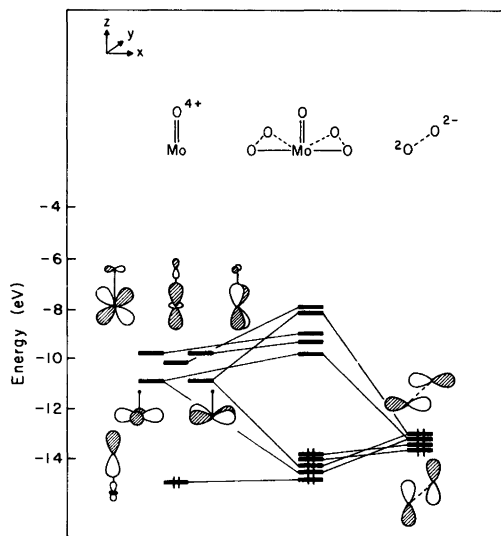


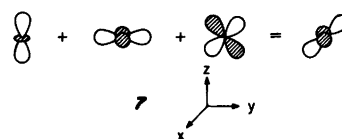
Fig. 1. The interaction diagram for the formation of MoO(O₂)₂ from MoO⁴⁺ (to the left) and 2 O₂²⁻ (to the right).

this is the angle between the lobes of the xy and x^2-y^2 orbitals. We found by variation of the angle between the oxygens in the peroxy groups that an angle of 54° gave the lowest energy. By the interaction of the MoO^{4+} and $2(\text{O}_2)^{2-}$ fragments, the oxygen orbitals with z character become the HOMO and 2nd HOMO of the system.

Fig. 2 shows the shape of the frontier orbitals. The expected splitting with the d orbitals of molybdenum as the unoccupied MOs and the p orbitals of oxygen as the occupied MOs is easily seen.

The second to fifth LUMOs of $\text{MoO}(\text{O}_2)_2$ are mainly of yx , xz , xy , and z^2 character, respectively, as shown in Fig. 2. The LUMO is more complex and is a combination of x^2-y^2 , z^2 and yz components. The product of the addition of these three components is shown below in 7, where the addition has been performed in a coordinate system rotated 90° relative to the coordinate system in Fig. 2. Contour plots of the LUMO in the xy and yz planes as well as the HOMO and the 3rd HOMO in the xz plane are shown in Fig. 3.

The contribution of x^2-y^2 , z^2 and yz components to the LUMO is 41%, 11% and 31%, respectively. The shape of the LUMO shown above as the sum of x^2-y^2 , z^2 and yz components is easily seen in Fig. 3b.



Though the empty orbitals of this Mo(VI) complex have been pushed up by interactions with the oxo and peroxy ligands they still retain acceptor character and are available for interaction with further ligands. We probed this with an approaching simple model base, H^- . Equatorial and axial bonding is available, using primarily the LUMOs of x^2-y^2 and z^2 symmetry. This helps us understand the structures of $\text{MoO}(\text{O}_2)_2\text{L}^1\text{L}^2$ (L^1, L^2 = donor ligands such as pyridine, *N,N*-dimethylformamide, hexamethyl phosphoric triamide (HMPA) or water) complexes, e.g. $\text{MoO}(\text{O}_2)_2 \cdot \text{HMPA}$ Py, **8a**¹⁵ and $\text{MoO}(\text{O}_2)_2 \cdot (+)\text{-MeCHOH-CONMe}_2$, **8b**.¹⁶

In order to anticipate our subsequent investigation of the epoxidation mechanism it is appropriate here to comment on the interaction of the low lying empty d block of $\text{MoO}(\text{O}_2)_2$ with π type orbitals, e.g. those found in an alkene. It seems obvious from the frontier orbitals shown in Fig. 2 and the X-ray structures that π electron donors bind at the metal. Furthermore, it appears from Figs. 2, 3 and the X-ray structure analysis of $\text{MoO}(\text{O}_2)_2$ complexes, **8**, that there are two binding sites for an alkene at the metal center: an equatorial coordination of an alkene, **9**, and an axial one, **10**.

Bonding, rotational barriers and conformational preferences of ethylene complexes have been studied recently in detail,^{17,18} so an extended investigation will not be carried out here; it is our goal to focus on a mechanistic investigation of the epoxidation reaction. Before proceeding to the interaction of the π orbital of an alkene with the empty d orbitals of the metal, let us determine if there is a preferred orientation of the alkene in

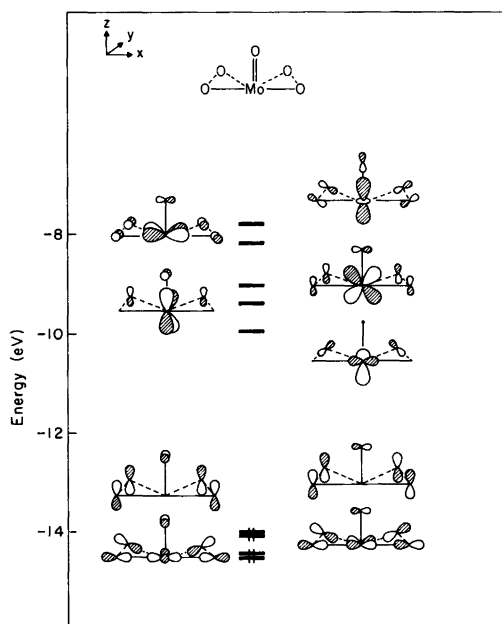
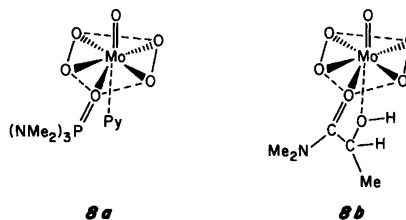


Fig. 2. The valence orbitals of $\text{MoO}(\text{O}_2)_2$.



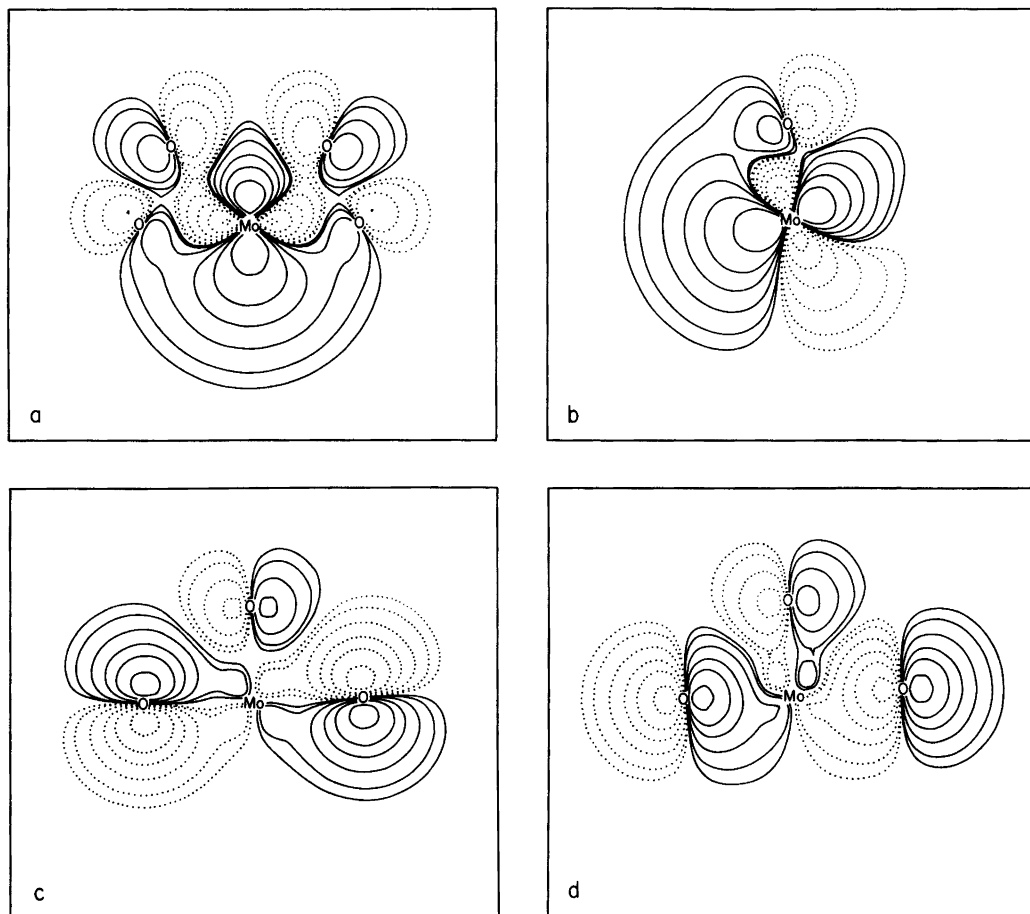
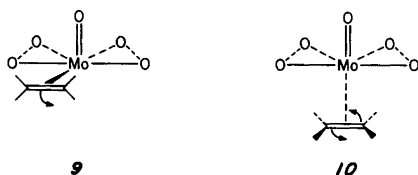


Fig. 3. Sketches of the valence orbitals of $\text{MoO}(\text{O}_2)_2$. The contour levels of ψ are 0.2, 0.1, 0.055, 0.025, 0.01 and 0.005. The LUMO is drawn in the xy plane (3a) and yz plane (3b); the HOMO in the xz plane (3c) and the third HOMO in the xz plane (3d).

the two $\text{MoO}(\text{O}_2)_2 \cdot (\text{C}_2\text{H}_4)$ complexes, **9** and **10**. Fig. 4 shows the change in total one-electron energy as a function of the rotation angle θ around the center of the double bond $\theta=0^\circ$ corresponding to the orientation shown in **9** and **10**. The calculations have been performed at a distance of



2.0 \AA between the metal and the center of the double bond which corresponds to $\text{Mo-C} = 2.13 \text{ \AA}$.

It appears from Fig. 4 that the total energy of complex **9** is always lower than that of complex **10**. The curve for **9** has a double minimum: one for the ethylene parallel to the molybdenum-peroxo bond and one parallel to the molybdenum-oxygen bond, of which the latter is found to be the more stable by 0.73 eV . For the ethylene in the axial position, the minimum is found for a rotation of 90° , which corresponds to an orientation of the ethylene perpendicular to the $\text{O}^2\text{-Mo-O}^5$ orientation. The two low energy conformations

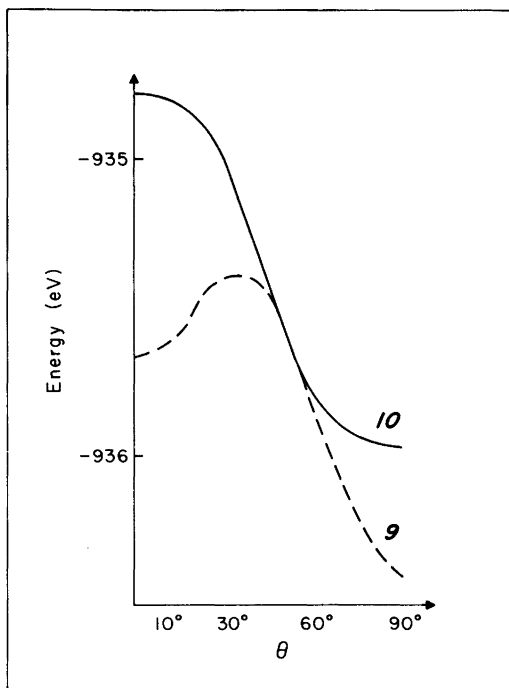
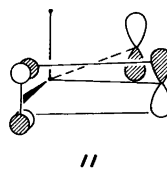


Fig. 4. The change in total energy for a rotation of ethylene in the equatorial (dashed line) and axial position (solid line) in $\text{MoO}(\text{O}_2)_2$.

of the complexes are shown in $9a$ and $10a$.

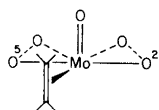
More detailed consideration of the various interactions, not presented here, shows that the reasons for the preference for ethylene equatorial binding may be traced to more favourable σ and π interactions for an ethylene in that geometry. These studies of the preferred orientation of an ethylene in the coordination sphere of $\text{MoO}(\text{O}_2)_2$ lead naturally to the two suggested epoxidation mechanisms, (A) and (B). The HOMO and second HOMO of $\text{MoO}(\text{O}_2)_2$ are located on the peroxy oxygens (Fig. 2) and are antisymmetric with respect to the molybdenum per-



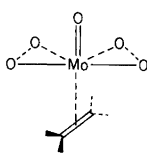
oxy plane. They are thus set up for an interaction with the antisymmetric π orbitals (π^*) of ethylene, 11 (here only shown for the left part of the $\text{MoO}(\text{O}_2)_2$ fragment). This obviously leads into mechanism (A).

The other mechanism, (B), proceeds from ethylene in an equatorial parallel position at the metal center by a slipping motion towards oxygen. The 3rd and 4th HOMO of $\text{MoO}(\text{O}_2)_2$ are molybdenum-peroxide bonding orbitals, mainly located on the O_2 , and these, as well as the lone pair on the peroxygens in the xy plane located at lower energies, might be able to interact with the π^* orbital of ethylene as shown below in 12 (only shown for the left part of the $\text{MoO}(\text{O}_2)_2$ fragment). The orientation of ethylene at the metal center corresponds to the minimum at 0° of the lower curve in Fig. 4.

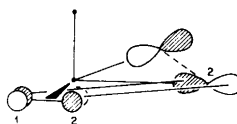
A slipping motion leads to a three-membered reaction viewpoint. In relation to this mechanism, the dioxometalocycle, 3 as the intermediate suggested by Mimoun *et al.*^{2,4} was also investigated from a frontier orbital point of view to see if the orbitals are set up for an intramolecular 1,3-dipolar cycloreversion. In order to simplify mechanism (A), we divided it into two steps as shown in Scheme 2. The first step is a slipping motion of the ethylene in a perpendicular orientation relative to the molybdenum peroxy plane ($6a$) toward oxygen no. 2 at a distance of 2 \AA from the bond connecting molybdenum and oxygen no. 2 (O^2). The second step, movement of O^2 with fixed molybdenum-oxygen bond length towards the ethylene, leads to $6a'$. The change in energy for the system for the first step as a function of the slipping distance, s , is shown in Fig. 5.



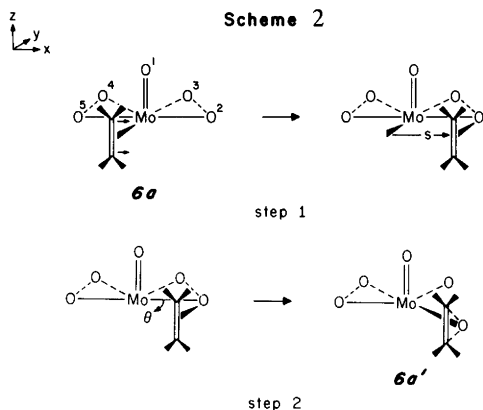
$9a$



$10a$



12



The total energy of the $\text{MoO}(\text{O}_2)_2 \cdot \text{C}_2\text{H}_4$ system increases with the slipping process and reaches a maximum when the ethylene is "in front of" the oxygen. The increase in energy can be traced to a decrease in overlap between the π orbital of ethylene and molybdenum in $\text{MoO}(\text{O}_2)_2$. At the same time, the ethylene $\pi^* - p_z$ of O^2 overlap (the overlap indicated in 11) increases. In the initial stages of the slipping, the Mo-O overlap populations also follow the anticipated trend: Mo-O² is

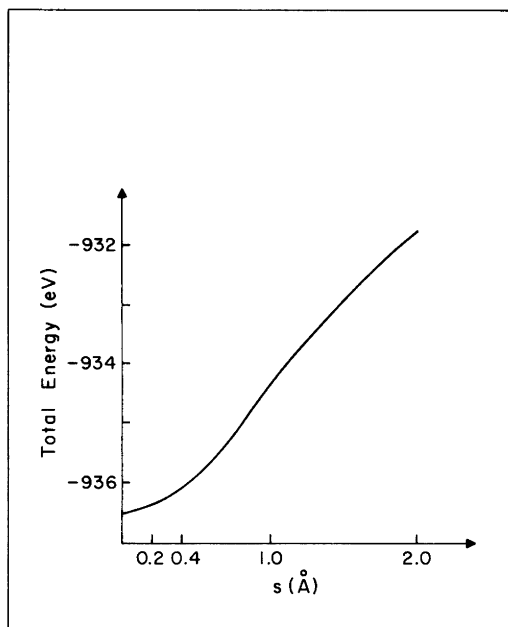


Fig. 5. The change in total energy for step 1 in mechanism (A); s is the slipping distance.

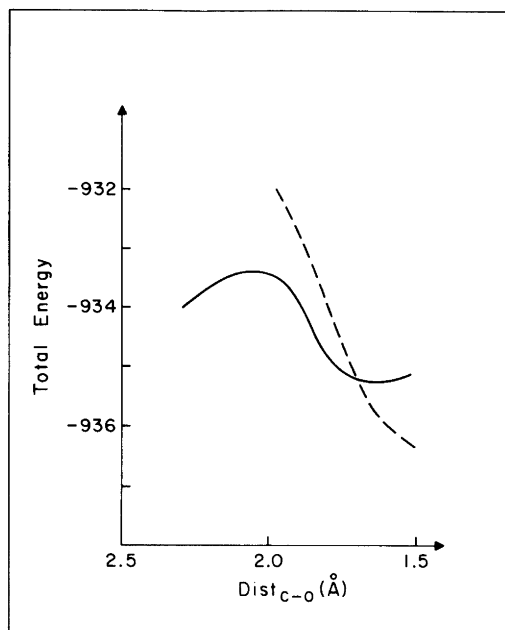


Fig. 6. The change in total energy for step 2 in mechanism (A). The solid curve is with $s = 1.1$ Å; the dashed curve is with $s = 1.8$ Å.

weakened and Mo-O³ is slightly strengthened. These tendencies do not persist as the slipping continues past 1 Å, but then we must be in a very unrealistic part of the surface.

Let us now continue with step two, movement of one of the peroxo oxygens toward the ethylene. Two calculations are shown in Fig. 6, one (solid curve) with the starting point being ethylene slipped by a moderate amount, 1.1 Å, the other with the ethylene slipped so it is "in front of O²". We are now clearly on the downhill side of the reaction. C-O bonds are forming rapidly (this is also indicated by computation of the C-O overlap populations). This is a consequence of the same ethylene $\pi^* - \text{O}^2 p_z$ interaction we have alluded to earlier. The second stage of reaction proceeds at lower energy if one doesn't slip the ethylene too much (solid versus dashed line in Fig. 6). But eventually one wants to form the C-O² bonds, so the curve derived from far-slipping ethylene ("in front of O²") decreases further.

What is indicated is a reaction path that combines steps 1 and 2 of Scheme 2. The extended Hückel method is not very good at deriving de-

tailed reaction paths, and the reaction, one in which several distances change, is not particularly well suited for the method. Nevertheless, we did try a calculation of a surface allowing steps 1 and 2 to proceed simultaneously. The result is shown in Fig. 7. Note that the reactant minimum is part way along coordinate 2; this is the result of an inadequate prediction of the O-O separation by extended Hückel. From the reactant minimum, the path combines motion of O^2 and slipping ethylene to give a product with an activation energy computed to be ~ 1.5 eV.

Let us now perform a similar analysis for mechanism (B). This mechanism will also be divided into two steps: a slipping motion of ethylene parallel to the molybdenum peroxy bond at a distance of 2 \AA from the bond connecting molybdenum and O^2 (step 1, Scheme 3); and a movement of O^2 towards the ethylene (step 2, Scheme 3) leading to $6b'$. The change in energy for the system as a function of the slipping distance, s , is shown in Fig. 8. It appears from Fig. 8 that there is a small decrease in the total energy for the $\text{MoO}(\text{O}_2)_2 \cdot \text{C}_2\text{H}_4$ system for a slipping until 0.7 \AA , after which an increase in energy is observed. The flat energy (even, slightly attractive region) in the early stages of the slipping is interesting. It is due to $\text{C}^2\text{-O}^2$ bonding (not shown here) growing along this coordinate. It should also be noted that even in the unslipped conformation there is already some $\text{C}^2\text{-O}^2$ bonding. The increase in energy observed here is slightly lower than that found in mechanism (A) Fig. 5). The slower energy increase observed here can be traced to the Mo-C^1 bonding, which, compared with the Mo-C^1 (or C^2) bonding in mechanism

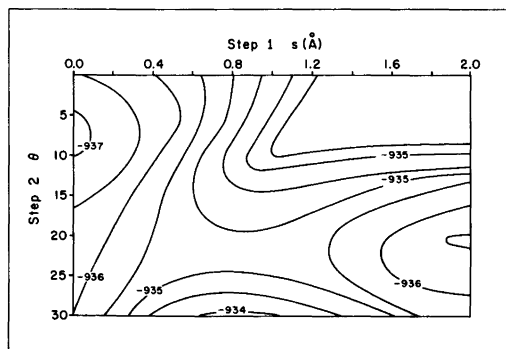
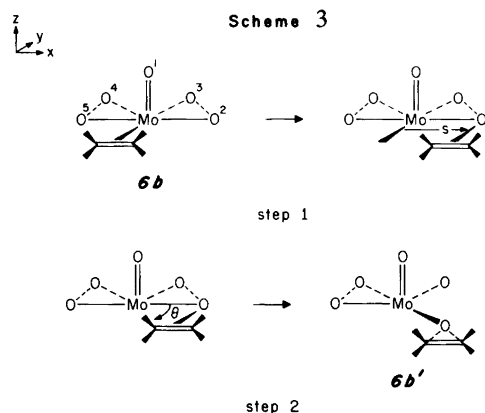


Fig. 7. Energy surface for mechanism (A).



(A) is better maintained. At the same time the ethylene $\pi^*\text{-p}_x$ of O^2 (the overlap indicated in $I2$) increases. The Mo-O overlap populations show the same trends as in mechanism (A).

Construction of an energy surface for mechanism (B) (not shown here) gives a surface similar to the one shown for mechanism (A) in Fig. 7. The energy minimum is here found at a slipping distance at about 1.6 \AA and a movement of O^2 about 22° ; the energy of this minimum is about

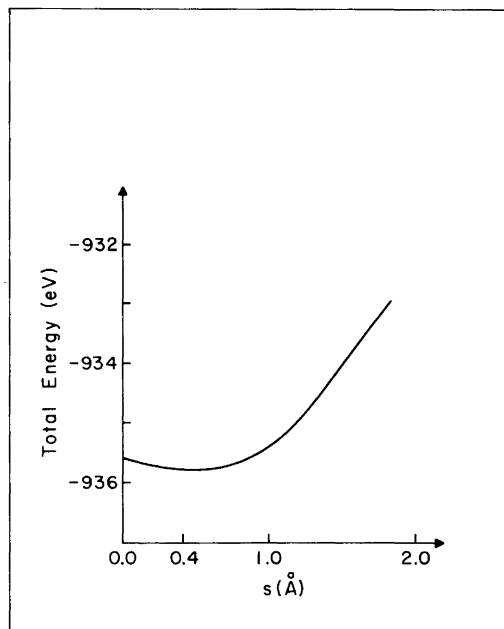


Fig. 8. The change in total energy for step 1 in mechanism (B).

the same as the minimum found for mechanism (A). The activation energy for mechanism (B) is found to be about 0.8 eV, which is about half that found for mechanism (A). The lower activation energy for mechanism (B) perhaps derives from the difference in energy of the two starting points for the reaction (compare the energies of *6a* and *6b* in Fig. 4). We do not consider the calculations sufficiently reliable to really distinguish between mechanisms (A) and (B) – perhaps both are operating.

Let us now try to analyze the dioxometalocycle *3*¹⁹ to investigate its eventual reaction leading to the epoxide and MoO₂(O₂). The epoxidation is here believed to take place via an intramolecular, 1,3-dipolar cycloreversion.^{2,4} Calculation of the total energy for different geometries of *3* gives energies which are at least 3–4 eV higher than those found for the transition state in mechanism (A). A calculation of the frontier orbitals of *3* (v. Scheme 1) reveals that these are not immediately set up for an interaction between O² and C¹. The only orbitals which are in position for interaction are occupied and will then lead to a repulsion. The calculated atomic net charges on these two atoms are both negative and of the same size, which also might lead to an additional repulsion.

We also studied a potential energy surface for formation of the epoxide from *3*. The transition state for this reaction brings us several eVs higher still than the dioxometalocycle, so we do not see it as competitive, at least our calculational method does not make it so, with the previously discussed paths. It appeared to us that the most probable mechanism for the MoO(O₂)₂ epoxidation of alkenes was mechanism (A) or (B), the perpendicular or parallel slipping motion of the alkene leading to a concerted reaction of the alkene with one of the peroxy oxygens, *11* or *12*.

The mechanism suggested here is in accord with the experimental observations found by Mimoun⁴ and others,⁶ that the first step is a coordination complex between the alkene and the molybdenum in MoO(O₂)₂. We have found that the coordination of the alkene to the molybdenum takes place with some electron donation from the π orbitals of ethylene to the empty d block of molybdenum, in accordance with the experimental results.^{4,6}

Beyond the calculations on the epoxidation by peroxy acids¹¹ mentioned earlier, some interest has also been devoted to the transition metal

catalyzed epoxidation: Goddard *et al.*²⁰ have studied hydrocarbon oxidation by high valent group VI oxides and there included the formation of epoxides from alkenes. The oxidizing agent was there chromyl chloride (CrO₂Cl₂) which reacted with alkenes to give either carbonyls, epoxides or the precursor to a chlorohydrin.²¹ The theoretical investigations on the chromyl chloride oxidations concentrated on the energetics of the intermediates, and the formation of the different products were discussed in relation thereto.²⁰ Recently, Bach *et al.*²² studied the frontier orbitals of a vanadium complex¹³ related to (dipic) VO(OOt-Bu)H₂O, *14*, which has recently been characterized by X-ray diffraction.²³ The frontier orbitals there were used to discuss the reaction with an alkene.

We have here tried to give a coherent theoretical model for the epoxidation of alkenes by η^2 peroxy complexes of group VI transition metals. It has been found that the most stable orientation of the alkene at the transition metal center is parallel to the transition metal-oxo bond – which means perpendicular to the transition metal peroxy plane. By a slipping motion of the alkene from the two orientations at the transition metal center (perpendicular or parallel to the transition metal peroxy plane) towards one of the peroxy oxygens, a favorable interaction between the π^* orbital of the ethylene and a lone pair on the oxygen becomes possible. On the basis of total energies and overlap populations, we suggest these mechanisms as likely ones, compared with the dioxometalocycle mechanism, for this type of epoxidation reaction. This mechanism involves first the binding of the alkene to the transition metal center, in accord with the first step suggested by Mimoun, whereas the next step differs from his suggestion. But a three-membered ring transition state, as suggested here, resembles the intermediate suggested by Sharpless.

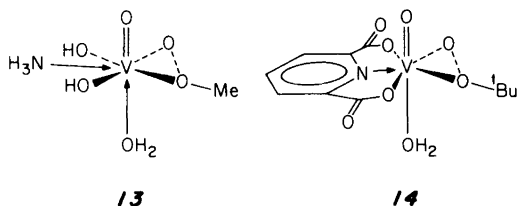


Table 1. Parameters used in extended Hückel calculations

Orbital	H_i	Exponents	ζ_2
		ζ_1^a	
H 1s	-13.6	1.3	
C 2s	-21.4	1.5	
2p	-11.4	1.325	
O 2s	-32.3	2.20	
2p	-14.8	1.975	
Mo 5s	-8.77	1.956	
5p	-5.60	1.921	
4d	-11.06	4.542 (0.58986) ^a	1.901 (0.58986)

^aCoefficients and exponents in a double-zeta expansion. All calculations were performed using the extended Hückel method.⁹ The bond lengths and angles for MoO(O₂)₂ have been taken from the MoO(O₂)₂L'L² complexes.^{12,13}

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