

Oxygen Transfer to Ethylene Catalyzed by the Ag(110) Surface: Possible Adsorption Sites for Molecular and Atomic Oxygen and a Model for the Oxygen-Transfer Step[†]

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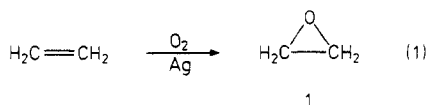
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Different adsorption sites for molecular and atomic oxygen on a silver surface and the epoxidation of ethylene have been studied by use of extended Hückel calculations. Several types of adsorbed molecular oxygen on an Ag(110) surface have been considered, an end-on adsorption on top of silver, a peroxidic adsorbed molecular oxygen, either adsorbed on a silver atom on the surface or bound to one in the second layer, and finally molecular oxygen located in the grooves along the [110] and [001] directions. For atomic adsorbed oxygen four types of geometries have been considered: two adsorption geometries on top of a silver atom, one on the surface and one in the second layer, and two bridging positions, one between two silver atoms in the [110] direction and the other in the [001] direction. The calculations indicate that possible adsorption sites for molecular oxygen are end-on or parallel to the surface located in the [110] or [001] direction; for atomically adsorbed oxygen the adsorption on top of a silver atom on the surface, or bridging between two silver atoms in the [110] direction, is favored. Transfer of the oxygen atom from some of the different types of adsorbed molecular and atomic oxygen has been studied. It is pointed out that a possible candidate for the active oxygen-transfer species can be an atomic oxygen bound to a silver atom on the surface. The transfer of the oxygen atom from an oxo-silver species to ethylene takes place by an initial interaction of the oxygen with one of the carbons in ethylene. This particular transfer, as well as several from other types of both molecular and atomic adsorbed oxygen, are discussed in relation to experimental results and also in relation to the epoxidation of alkenes catalyzed by molecular complexes. The influence of chlorine on the adsorbed oxygen has also been studied.

The transfer of an oxygen atom from a silver surface to ethylene leading to ethylene oxide (1) (eq 1) is an important reaction in



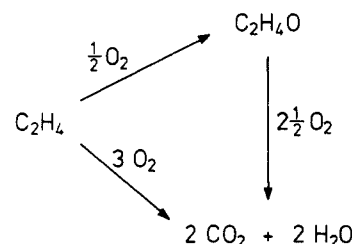
industry—a several billion dollar per year process.¹ The reaction also serves as a challenge to the academic field, as the different steps involved in the reaction path are not resolved, in spite of extensive investigations.²

The oxidation of ethylene to ethylene oxide as outlined in eq 1 is not the only reaction that occurs when ethylene and oxygen are exposed to a silver surface. Scheme I illustrates the dominant reaction paths in ethylene epoxidation catalyzed by a silver surface. Besides the epoxidation reaction, combustion of ethylene or ethylene oxide to carbon dioxide and water is also observed.^{2a-d} The selectivity of the reaction (defined as the number of moles of ethylene oxide produced divided by the total ethylene reacted) has been found to be about 45% on clean silver catalysts.³ However, in the presence of either electronegative moderators such as chlorine or the electropositive alkali and alkaline-earth metals the selectivity can be increased to 75–87%.²

The use of oxygen on silver surfaces for epoxidation is a unique reaction only for ethylene.² Other alkenes as substrates lead to low yields of the corresponding epoxides, and little use of silver catalysis has been made for other alkenes. It should, however, be noted that styrene with no β -hydrogen has been reported to give good yields of styrene oxide^{4a} and that norbornene is converted to norbornene oxide by atomic oxygen on Ag(110).^{4b}

The silver surface catalyzed epoxidation of ethylene can be considered as a two-step process: an activation of molecular oxygen for the oxygen donation step followed by the transfer of an oxygen atom to ethylene. To obtain an understanding of the mechanism of ethylene epoxidation catalyzed by silver surfaces, one is then faced with the following questions: (i) How is mo-

SCHEME I



lecular oxygen adsorbed on a silver surface? (ii) What is nature of the oxygen that is transferred to the ethylene? (iii) How is the oxygen transferred to the ethylene? Our purpose in the following work will then be to address these questions.

Let us first briefly review some of the experimental results relevant to the analysis presented here. Many surface science studies, particularly on the Ag(110) face, have focused on identifying the oxygen species directly responsible for epoxidation. Three types of oxygen have been observed when molecular oxygen is exposed to an Ag(110) surface: molecular, atomic, and sub-surface oxygen.²

High-resolution electron energy loss spectroscopy (HREELS) has been used for the identification and characterization of the molecular oxygen species on the Ag(110) surface.^{2d,5} The molecular nature of some of the adsorbed oxygen has also been

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[†] Dedicated to our friend Richard Netter on the occasion of his 70th birthday.

verified by using temperature-desorption experiments with a mixture of $^{16}\text{O}_2$ and $^{18}\text{O}_2$, in which no scrambling was observed below 170 K.^{5,6} X-ray photoelectron spectroscopy (XPS) of molecular oxygen on Ag(110) shows only a single peak, which leads to the conclusion that the oxygen molecules lie flat on the surface, since end-on adsorption would have produced two O(1s) photoelectron peaks.^{7,8}

Molecular orbital cluster calculations of molecular oxygen on Ag(110) revealed two reasonable structures for molecular oxygen, both lying flat on the surface. For one the oxygen molecule is parallel to the direction of the groove, and for other it is located perpendicular to the groove with a preference for the latter.⁹ Recent near-edge X-ray adsorption fine structure (NEXAFS) studies show that the primary, and hence most stable, form of adsorbed molecular oxygen on Ag(110) is with the O-O axis parallel to the plane of the surface with the O-O bond vector along the [110] direction.¹⁰ Generalized valence bond and configuration interaction calculations of the chemisorption of molecular oxygen on Ag(110) with a 24-atom supercell cluster model for the Ag(110) surface show that the O-O axis parallel to the grooves, in the [110] direction, is preferred,¹¹ which agrees with the NEXAFS results.^{10a} However, electron-stimulated-desorption ion angular distribution (ESDIAD) studies favor a site with a component of the O-O bond along the [001] azimuth.¹²

Atomic oxygen can be formed by dissociative cleavage of molecular oxygen on the silver surface. Atomic oxygen on the [110] surface has been identified by several different techniques.^{2,c,d} Low-energy electron diffraction investigations and ion scattering experiments have indicated that oxygen atoms are adsorbed in the grooves of the [110] surface,¹³ but it has also been proposed that oxygen can be absorbed in other ways.^{8,14} A few theoretical calculations have also been performed on atomic oxygen bound to silver clusters.¹⁵

The third type of oxygen suggested to be present on a silver surface is subsurface oxygen. By its very nature a detailed characterization of such a species by surface-specific techniques is difficult. Nevertheless its presence has been verified by several groups.^{5,16}

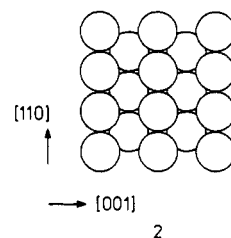
As to the oxygen-transfer step, there has been a great debate about the nature of the species involved—molecular vs atomic oxygen.¹⁷ If it is assumed that only molecularly adsorbed oxygen can give epoxide upon reaction with ethylene and that the remaining oxygen atoms cannot recombine on the surface, six oxygen molecules can produce six molecules of ethylene oxide. Because only one oxygen atom per oxygen molecule is incorporated into epoxide, six oxygen atoms will remain adsorbed onto the silver surface. As the reaction can continue "indefinitely", these oxygen atoms must be removed so as not to block the surface. More reactant ethylene will have to be used to remove atomic oxygen in a nonselective complete combustion reaction. Six oxygen atoms are needed for the total oxidation of ethylene (see Scheme I). These arguments lead to the prediction of a maximum initial selectivity of 6/7, if molecular oxygen provides the reaction path to the epoxide. Few experimental studies have found selectivities

larger than 6/7, which is one of the main reasons why this mechanism has found wide support.² Further evidence for a mechanism involving a peroxy species comes from IR studies of the interaction of adsorbed oxygen with ethylene, in which bands corresponding to a surface peroxy species $\text{H}_2\text{C}-\text{CH}_2-\text{O}-\text{O}-\text{Ag}_{\text{surf}}$ have been assigned.¹⁸

The case for the involvement of atomic oxygen in the epoxidation step arises from several types of experimental studies.² It has been shown that it is weakly adsorbed oxygen which yields the epoxide,^{2d,19} and that this weakly adsorbed oxygen is found for $\text{O}/\text{Ag} > 0.5$.²⁰ Furthermore, it has been shown that epoxide is formed in the reaction of ethylene with AgO .^{19a} Oxygen-labeling experiments have also demonstrated that atomic oxygen on the surface can be incorporated into the epoxide.^{2d,21}

The epoxidation of ethylene catalyzed by a silver surface with molecular oxygen as the oxidant is not stereoselective. Epoxidation of *cis*-1,2-dideuterioethylene leads to a substantial amount of the *trans*-epoxide, and the corresponding *trans*-alkene produces some *cis*-epoxide.²² In one study, about 70% retention^{22a} of the original conformation was found in the produce epoxide, whereas others have observed that the epoxide products are nearly equilibrated.^{22b,c}

In the present study we will try to elucidate how molecular and atomic oxygen can be adsorbed onto a silver surface in order to determine the electronic nature of the adsorbed species and to examine how the oxygen-transfer step to ethylene can take place. Also, we will consider the influence of moderators, such as chlorine, on the electronic nature of the oxygen that is transferred to the ethylene. For these purposes we will make use of extended Hückel calculations and the two-dimensional character of the system via the tight-binding approximation.²³ We are aware of the fact that the quantitative results obtained by extended Hückel calculations cannot be sufficiently trusted in studies where the formation and cleavage of several bonds are simultaneously involved. With regard to the adsorption of the electronegative species on a metal surface, as well as interaction between electronegative species and metals, the present method has been found able to provide us with useful information.²⁴ Furthermore, as our intention is to try to give a qualitative description of the oxygen-transfer step, extended Hückel calculations should be able to give us useful information about the reaction which allows the understanding of the epoxidation of ethylene catalyzed by the silver surface. As the Ag(110) surface shown in **2** has been shown to be a good model for the real



catalyst,²⁵ we have chosen this type of surface for the present study.

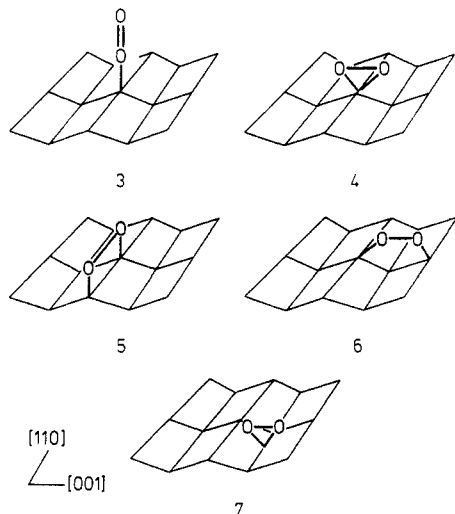
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Very recently Carter and Goddard published two papers concerning the energies involved in the silver-catalyzed epoxidation of alkenes using three silver atoms in an equilateral triangle as a model for the silver surface.²⁶ The 3-fold site of this silver cluster is believed to correspond closely to the analogous site on Ag(111).²⁶ On the basis of the study of the interaction of atomic and molecular oxygen with the silver cluster they proposed that a surface atomic oxy radical anion oxygen is the active oxygen species for forming the epoxide.²⁶

Adsorption of Molecular Oxygen on Ag(110)

For the adsorption of molecular oxygen on Ag(110) we have chosen to study five binding types: end-on 3, side-on with molecular oxygen bound to one silver atom, 4, bridging between two silver atoms, 5 and 6, and finally molecular oxygen located in the grooves of the surface, 7. Before proceeding to the adsorption



of molecular oxygen on the Ag(110) surface, let us start with the calculations of the density of states (DOS) for Ag(110).²⁷ With the parameters used here for a system with three layers of silver atoms, the Fermi level has been calculated to -10.69 eV. The d band is spread out over 2 eV from about -14 to -16 eV; the s molecular orbitals spread out on the vacuum side on the d band.

Let us start with the end-on adsorption of molecular oxygen of the Ag(110) surface, 3; besides the linear approach shown in 3, the oxygen might also be bent relative to the surface. It has been found that the end-on adsorbed molecular oxygen on Ag(110) surface exhibits a weak preference (2 kcal/mol) for being bent (130°). The bending of molecular oxygen is in agreement with the structure found for several mononuclear transition-metal superoxo complexes.²⁸ There is no preferred orientation of the bent oxygen relative to the silver surface.

The binding energy and overlap populations for molecular oxygen to the Ag(110) surface for the different approaches shown in 3–7 are given in Table I. The a geometries refer to an orientation of molecular oxygen along the [001] direction, and the b geometries to an orientation along the [110] direction. The b geometries imply that the molecular oxygen in 6b and 7b is lying along the grooves. The variation in binding energy for molecular oxygen on the Ag(110) surface is of the same magnitude as, e.g., the variation in binding energy for the different adsorption sites for NO on Ni(111).^{24a} Upon end-on adsorption of molecular oxygen in a bent form relative to the Ag(110) surface, the overlap population between the oxygens decreases from 0.817 to 0.433; the bond character changes roughly from double to single. The orbitals leading to interaction can be traced to a combination of

TABLE I: Binding Energies, Fermi Levels, and Ag–O and O–O Overlap Populations for Ag(110), O₂, and the Different Types of Adsorbed Molecular Oxygen, 3–7^a

	binding energy, ^b eV	ϵ_F , eV	overlap population	
			Ag–O	O–O
Ag(110)		-10.62		
O ₂				0.817
3	5.12	-11.02	0.289	0.433
4a	4.57	-11.02	0.085	0.442
4b	4.49	-11.01	0.083	0.442
5	5.43	-10.99	0.128	0.452
6a	5.16	-10.90	0.240	0.445
6b	3.11	-10.69	0.035	0.449
7a	3.74	-10.59	0.208	0.457
7b	3.52	-10.72	0.141	0.463

^a The a geometries refer to an orientation of molecular oxygen along the [001] direction, and the b geometries refer to an orientation along the [110] direction. ^b Binding energy = $E(\text{Ag slab}) - E(\text{O}_2 \text{ layer}) - E(\text{Ag} + \text{O}_2)$.

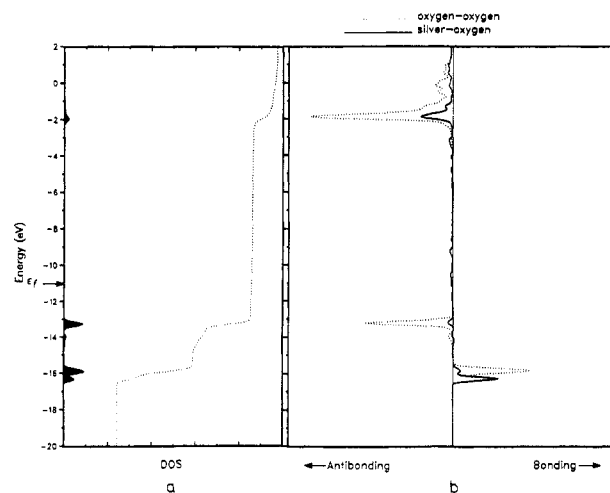
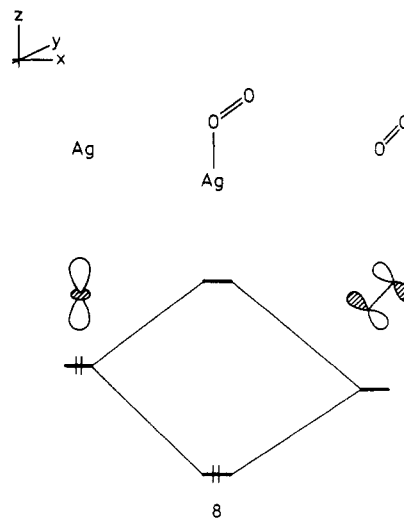


Figure 1. (a) Total DOS for 3. The contribution from molecular oxygen is shown as the shaded area. The dotted line is the integration of the contribution from molecular oxygen. (b) The crystal orbital overlap population (COOP) curves for the oxygen–oxygen bond (dotted line) and the silver–oxygen bond (full line).

s and d_{z^2} on silver and the π^* of molecular oxygen shown in 8 (vide infra). It turns out that the antibonding combination of the



interaction shown in 8 is located below the Fermi level of the silver surface. This antibonding combination will then be populated with electrons from the surface. The Ag–O antibonding interaction is readable from the crystal orbital overlap population (COOP) curve^{23c,29} shown as the full line in Figure 1b; the an-

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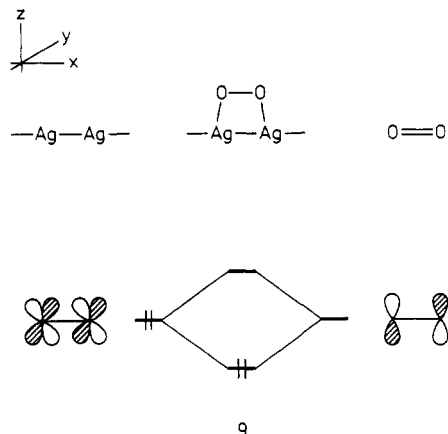
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tibonding character appears at about -13 eV. Figure 1 shows the total DOS for **3** with the contribution from molecular oxygen as the shaded area (a) and the O-O and Ag-O COOP curves (b).

The end-on adsorption of molecular oxygen gives rise to two new DOS features relative to the d block of the Ag(110) surface, one split peak located at -16 eV below the d block and one located at about -13.3 eV above the d block. From the O-O COOP curve (dotted line in Figure 1b) the latter is seen to be antibonding, thus assigned to the $\pi^*_{\text{O-O}}$ orbital, and the former, being O-O bonding, is mainly derived from the $\pi_{\text{O-O}}$ orbital. The two π peaks are involved in Ag-O bonding as seen from the Ag-O COOP (full line in Figure 1b). The end-on adsorption leads to net transfer of 1.71 electrons from the silver surface to the molecular oxygen fragment with 1.02 electrons located at the terminal oxygen.

Let us now continue with the other approaches of molecular oxygen to Ag(110), **4-7**. It appears from Table I that the largest binding energy is found for molecular oxygen bound to two silver atoms in the same row, **5**. Slightly less favorable is the molecular oxygen bound to two silver atoms in two different rows, i.e., across the grooves, **6a**. These three types of adsorption are more than 0.5 eV more stable than the others studied, so we will concentrate our attention on **5** and **6a**, although we cannot exclude the other adsorption types available on the surface. A previous molecular orbital cluster study of molecular oxygen on Ag(110) favored an O_2 geometry above the long 2-fold bridge site with O-O bond oriented parallel to the surface along the [001] azimuth,⁹ whereas the GVB calculations favor O_2 along the [110] azimuth.^{11a} It should also be mentioned that similar binding of molecular oxygen to two transition metals has been observed in several binuclear transition-metal complexes.²⁸

Two main types of interaction between molecular oxygen and the Ag(110) surface are involved in producing the chemisorptive bond in **5**. One is outlined in **9**, where the interaction takes place



between the d_{xz} orbital at the silvers and the π^* orbital of molecular oxygen, leading to a population of both bonding and antibonding combinations because the latter is again located below the Fermi level of the surface. The other interaction takes place between the other π^* orbital of molecular oxygen (locally p_y) and silver d_{yz} . Both π^* orbitals of molecular oxygen are in the case of a triplet state populated with one electron (not shown in **9**), but our calculation does not take the spin state of molecular oxygen into account.

The contribution of molecular oxygen in **5** to the total DOS and the O-O and Ag-O COOP curves are shown in Figure 2. The curves in Figure 1 (for **3**) and those shown in Figure 2 (for **5**) are more or less alike; the only difference for the DOS curves is that the lower part of the oxygen contribution to the total DOS in Figure 2a is located about 0.5 eV lower in energy compared with Figure 1a. The difference between the COOP curves of **3** and **5** is that the antibonding Ag-O part located at about -13.3 eV in Figure 1b now has changed to a bonding one in Figure 2b at about -14.5 eV.

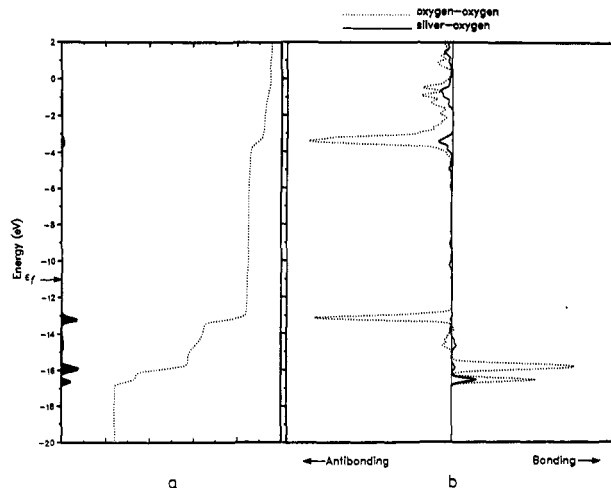
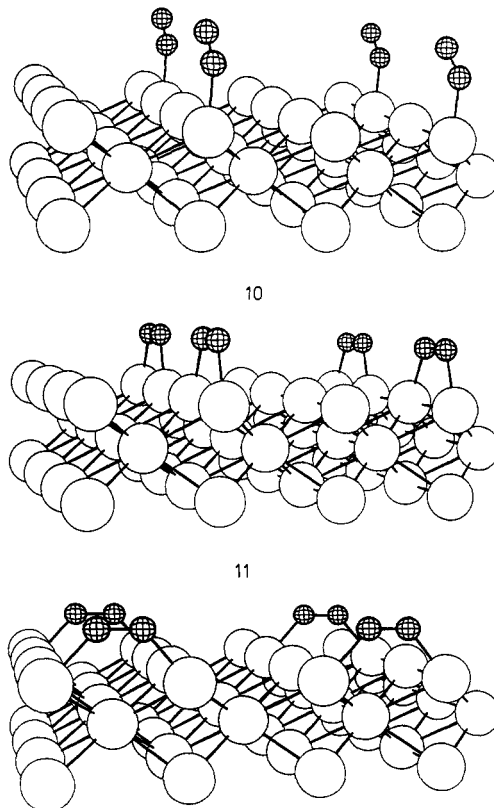


Figure 2. (a) Total DOS for **5**. The contribution from molecular oxygen is shown as the shaded area. The dotted line is the integration of the contribution from molecular oxygen. (b) The COOP curves for the oxygen-oxygen bond (dotted line) and the silver-oxygen bond (full line).

Moving from an adsorption of molecular oxygen to two silver atoms in the same row (**5**) to adsorption of molecular oxygen in two different rows (**6a**) does not change DOS and COOPs curves significantly from those shown in Figure 2. The trends are the same; the relevant curves are not shown here. Both adsorption types, **5** and **6a**, lead to a net transfer of 1.50 electrons from the silver surface to molecular oxygen.

The present results seem to favor **3**, **5**, and **6a** from a binding energy point of view as the most probable adsorption geometries of molecular oxygen to Ag(110), although the difference is not so substantial as to exclude the others. The two adsorption geometries **5** and **6a** could be those that are observed in the NEX-AFS¹⁰ and ESDIAD¹² studies.

A more detailed picture of the three preferred adsorption geometries, **3**, **5**, and **6** is shown in **10**, **11**, and **12** (the oxygens are lined).

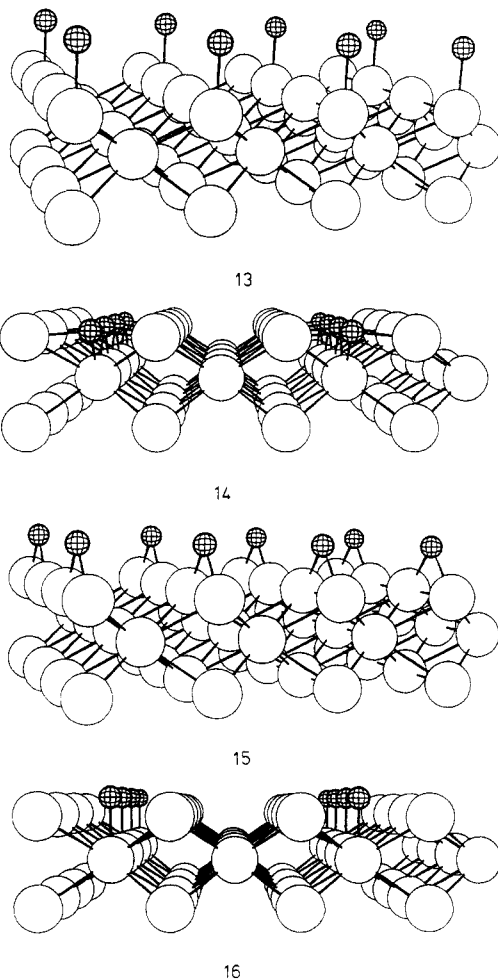


The net charge of the adsorbed molecular oxygen has in all cases been found to be between -1.50 and -1.71 . On the basis of the low O–O stretching vibration frequency found for adsorbed molecular oxygen on Ag(110) in comparison with other molecular oxygen reference compounds of varying formal charge,⁵ the formal charge of the adsorbed molecular oxygen has been extrapolated to -1.7 . This is in agreement with our calculated formal charge, but this should also be expected because of the back-donation of electrons from the silver surface to the π^* -antibonding oxygen orbitals. The latter are below the Ag Fermi level and so are mostly occupied.

The end-on coordinated molecular oxygen, **3**, should, by XPS, give rise to two peaks for the two different O(1s) electrons. Experimentally only one peak is found,⁷ which might make **10** less likely than **11** and **12**, as the oxygens in the two latter modes are equivalent. But we will not exclude **10** as a possible model for the active surface species on the basis of this result.

Adsorption of Atomic Oxygen on Ag(110)

For the adsorption of atomic oxygen on Ag(110) we have chosen to study four binding types: an oxo–silver species, **13**, two bridging species, **14**, across and, **15**, along the grooves, and oxygen bound in the grooves over a silver atom in the second layer, **16** (the oxygens are lined).



According to several investigations molecularly adsorbed oxygen on Ag(110) dissociates into atomic oxygen above 170 K.⁸ Considering the population of the π^* antibonding orbitals in chemisorbed molecular oxygen this is not surprising. The binding energies and overlap populations for two atomic oxygens per unit cell, for the different approaches shown in **13**–**16**, are given in Table II.

It appears from Table II that atomic adsorbed oxygen as **13** and **15** are about 2 eV more stable than **14** and **16**. All the calculations have been performed with a Ag–O distance of 2.1 Å, which is very similar to the bond length found useful by others:³⁰

TABLE II: Binding Energies, Fermi Levels, and Ag–O Overlap Populations for the Different Types of Adsorbed Atomic Oxygen on Ag(110), 13–16

	binding energy, ^a eV	ϵ_F , eV	Ag–O overlap population ^b
13	12.33	-11.39	0.280
14	10.45	-10.79	0.238
15	12.42	-11.25	0.190
16	10.69	-11.00	0.218

^a Binding energy = $E(\text{Ag slab}) - E(\text{O layer}) - E(\text{Ag} + \text{O})$. ^b The overlap population is taken to the nearest silver neighbor.

changing the Ag–O distance slightly does not exchange the ordering of the stability of **13**–**16**. The binding energy of atomic oxygen on the Ag(110) surface presented in Table II is exaggerated compared with the experimental results, but we believe that the trends of the stabilization reflect the possible candidates for atomic oxygen on the Ag(110) surface. The structure shown in **13** can be considered as an AgO species, whereas the one shown in **15** is Ag₂O-like.³¹ The Ag–O overlap population in **13** is calculated to 0.280, 0.238 in **14** between oxygen and each silver in the surface, 0.190 in **15** also between oxygen and each silver in the surface, and 0.218 in **16** between oxygen and silver in the second layer. Based on both the binding energy and overlap populations our calculations indicate thus **13** and **15** as prime candidates for how atomic oxygen is adsorbed on an Ag(110) surface.

The interaction leading to the Ag–O bond in **13** takes place mainly between the Ag d_{z^2} and s orbitals and the O p_z orbital. Also, the d_{xz} and d_{yz} orbitals on silver interact with the p_x and p_y orbitals on oxygen. Figure 3 shows the total DOS with the total contribution from the oxygens (Figure 3a), the contribution from only the oxygen p_x and p_z orbitals, Figure 3b and Figure 3c, respectively, and the COOP curve for the silver–oxygen bond (Figure 3d).

It appears from Figure 3a that the oxygen p levels are spread over an ~ 2.5 -eV region from ~ -13.5 to -16 eV. The interaction of silver d_{xz} with oxygen p_x creates the oxygen contribution to the DOS shown as the shaded area in Figure 3b (similar for silver d_{yz} with oxygen p_y), which are the $\pi_{\text{Ag-O}}$ and $\pi^*_{\text{Ag-O}}$ orbitals. The interaction of the silver d_{z^2} and s orbital with oxygen p_z leads to the $\sigma_{\text{Ag-O}}$ and $\sigma^*_{\text{Ag-O}}$ which are the lowest and highest part of the oxygen contribution to DOS (Figure 3c). The location of the bonding and antibonding character of the Ag–O bond is seen in Figure 3d. The net charge on oxygen in **13** is calculated as -1.74 , which is the same charge as found for the adsorbed molecular oxygen unit.

The contribution from the oxygens to the DOS for **15** is much like the curves shown for **13** (Figure 3) and leads to three separate levels, one right below and one above -16 eV and one between -13 and -14 eV. The oxygen directly below -16 eV is mainly related to interaction of the oxygen p_x orbital with two silver $d_{x^2-y^2}$ orbitals, and the oxygen contribution to the DOS found right above -16 eV is in a similar way related to the interaction of the oxygen p_y and p_z orbitals with the silver d_{xy} and d_{yz} orbitals, respectively. The Ag–O COOP curves show that the interaction between oxygen p_x orbitals and silver $d_{x^2-y^2}$ is responsible for the major part of the bonding between these atoms. The total charge on the oxygen is -1.32 . The COOP curve for the Ag–O bond for **15** does not show the splitting into σ and π bonding and antibonding character as **13** does. The antibonding character between silver and oxygen is located lower in energy in **15** when compared to **13**.

Our calculations of adsorbed molecular and atomic oxygen on Ag(110) leave us with several possibilities for the active oxygen donor species on a silver surface: end-on adsorbed molecular oxygen, **10**, bridging molecular oxygen, **11** and **12**, and both on-top and bridging atomic oxygen, **13** and **15**, respectively. As far as

(30) van der Hoek, P. J.; Baerends, E. J.; van Santen, R. A. *J. Phys. Chem.* **1989**, *93*, 6469.

(31) For the structures of AgO and Ag₂O see, e.g.: Wells, A. F. *Structural Inorganic Chemistry*; Oxford University Press: Oxford, 1962; pp 267, 460, 462, 882.

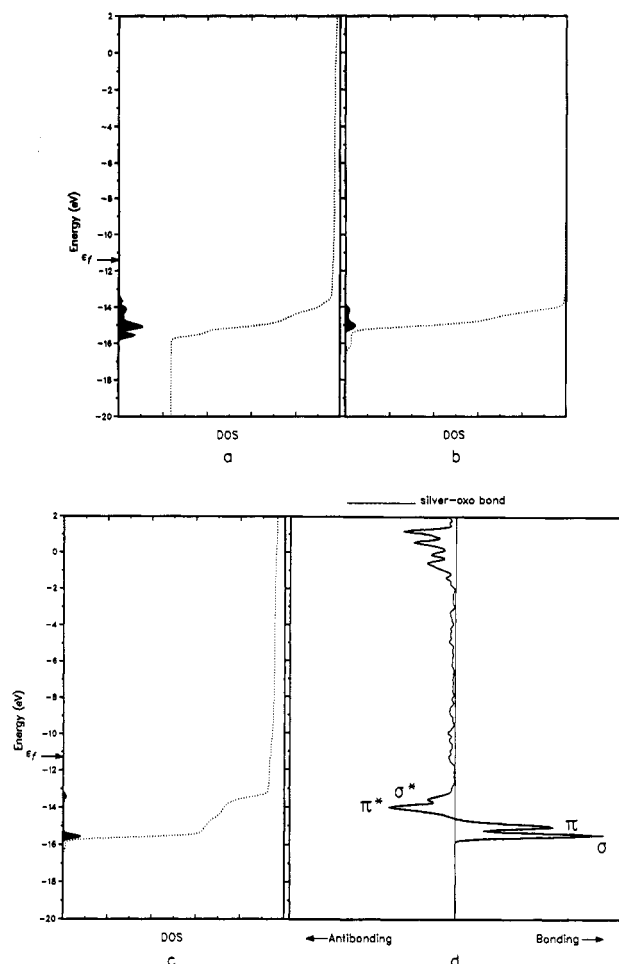


Figure 3. (a) Total DOS for **13**. The contribution from atomic oxygen is shown as the shaded area. The dotted line is the integration of the contribution from atomic oxygen. (b) The contribution from the oxygen p_x orbital. (c) The contribution from the oxygen p_z orbital. (d) The COOP curve for the silver-oxygen bond.

bonding is concerned, our calculations seem to favor atomic adsorbed oxygen. One should be aware that a direct comparison of stability of the two different types of adsorbed oxygen (atomic vs molecular) is not feasible with these type of calculations. However, strong bonding does not necessarily point the species that is involved in the catalytic act, i.e., in promoting the lowest activation barrier in a reaction. We think we must leave open the possibility of either an atomic or a molecular species being active in the catalysis.

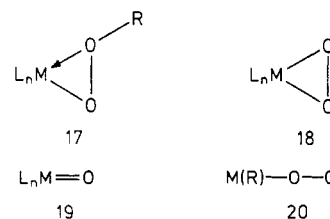
The two bridging molecular oxygen species, **11** and **12**, are interesting, since by dissociation of the oxygen-oxygen bond, they can lead to the on-top adsorbed atomic oxygen, **13**. Species **11** and **12** may then be the precursor adsorbed molecular oxygen species that might give the atomic adsorbed oxygen, **13**.

A Model for the Oxygen-Transfer Step

Before proceeding to the transfer of the oxygen from the silver surface of the ethylene, we find it appropriate to draw attention to the different mechanisms suggested for the epoxidation of alkenes catalyzed by molecular transition-metal complexes.^{2e,32} Our intention is to try to build a bridge from what is known about the epoxidation reaction catalyzed by molecular transition-metal complexes to the epoxidation of ethylene by oxygen on a silver surface.

Three main types of complexes are involved in the transfer of an oxygen atom from the reactive intermediate to an alkene: (i) transition-metal peroxide/peroxo complexes, **17**, **18**, (ii) oxo-transition-metal complexes, **19**, and (iii) peroxo radicals, **20**.^{2e,32-34}

(32) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981.



The transition-metal peroxide (peroxo) complexes are operative in the beginning of the transition-metal series, where the transition metal is in its highest oxidation state— d^0 making a coordination of the peroxide/peroxo group possible.^{2e} The oxo-transition-metal complexes act as catalysts from the middle toward the end of the transition-metal series and in some cases side by side with peroxo radicals.^{2e}

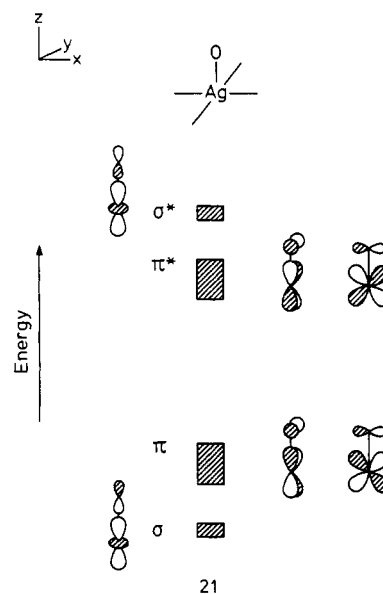
Some of the molecular and atomic oxygen species present on the Ag(110) surface are thus comparable to the molecular species, **17-20**. As far as we know, molecular species containing bridging molecular and atomic oxygen (comparable to **11**, **12**, **14**, and **15**) are not known to be directly involved in oxygen transfer to alkenes leading to epoxides.

If we assume that the oxygen species decisive in both molecular and surface epoxidation are similar, we end up with two main candidates for the active surface-oxygen-transfer species from our calculations: **10** and **13**.

In the molecular systems the oxo-transition-metal complexes have in particular been studied with porphyrins^{2e,32,34} and salens^{2e,35} as ligands. The active oxo-transition-metal complex is prepared from the transition-metal complex and an oxygen donor system. Some of these oxo-transition-metal complexes have a property that is comparable to oxygen on a silver surface—they transfer the oxygen atom to an alkene in a nonstereoselective way, as epoxidation of *cis*-alkenes gives a mixture of both *cis*- and *trans*-epoxides.^{2e,32,34,35}

The peroxo-radical complexes are also known from molecular systems; they add to alkenes giving epoxides, but this reaction is often accomplished by side reactions.³²

In the following we discuss the oxygen-transfer step to ethylene from several types of both molecular and atomic adsorbed oxygen on Ag(110). As a starting point we will use **13** as the active species; the frontier orbitals of the oxo-silver part of **13** are shown in **21**.

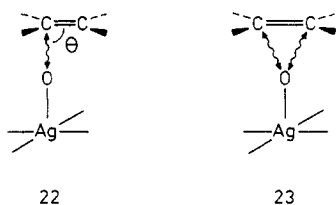


(33) See also: Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401.

(34) For a review about oxygen transfer catalyzed by transition-metal porphyrins see: Meunier, B. *Bull. Soc. Chim. Fr.* **1986**, 578.

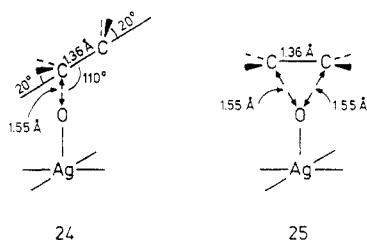
(35) (a) Siddall, T. L.; Miyaura, N.; Kochi, J. K. *J. Am. Chem. Soc.* **1985**, *107*, 7606. (b) Srinivasan, K.; Michaud, P.; Kochi, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 2309. (c) Koola, J. D.; Kochi, J. K. *J. Org. Chem.* **1987**, *52*, 4545.

Given the frontier orbitals of ethylene, π and π^* , two types of interaction between the oxygen in **13** and ethylene are possible. The first type of interaction is asymmetric and shown in **22** (with variable θ); the second, a symmetric is outlined in **23**. The



approach of the ethylene to the Ag–O bond depicted in **22** corresponds to interaction of the σ^* Ag–O orbital with the π^* of the ethylene, whereas the approach shown in **23** is an interaction of the π^* Ag–O orbital with the π^* orbital of ethylene. Besides the attractive interaction between high occupied MOs (HOMOs) at oxygen in **23** and the lowest unoccupied MO (LUMO) in ethylene, repulsive interaction between the Ag–O σ^* orbital and the HOMO of ethylene is also observed in **23**.

We have calculated the change in interaction energy for the two different approaches **24** and **25**. The relevant geometries of ethylene relative to the Ag–O fragment are shown below, where the carbon interacting with oxygen in **24** is assumed to be nearly tetrahedral:



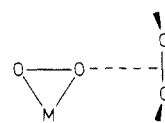
Our calculations show that **24** is 7–8 kcal·mol⁻¹ more stable than **25**. Bending the hydrogen up in **25** to make the carbons tetrahedral leads to an even greater destabilization of **25** relative to **24**. The overlap population of interest in the two systems are as follows. **24**: Ag–O, 0.242; O–C, 0.410; C–C, 0.942; **25**: Ag–O, 0.252; O–C, 0.367; C–C, 0.804. Without ethylene the Ag–O overlap population is 0.280. It appears from the overlap that the Ag–O bond in **24** is weakened slightly more than in **25** and that the O–C bond in **24** is stronger than in **25**. Both C–C overlap populations are reduced significantly compared to ethylene and correspond approximately to a C–C single bond. With these results favoring the unsymmetric intermediate, **24**, the accessibility of free rotation around the C–C bond is thus possible. This can allow for the previously mentioned change of the stereochemistry of the alkene during the oxygen-transfer step.²² Carter and Goddard have found that the interaction of one of the carbons in ethylene with the oxygen in their oxo-silver surface model system (like **24**) is favored by 5 kcal·mol⁻¹.²⁶ The approach **24** is comparable to the one suggested on basis of GVB-CCCI calculations.²⁶ van der Hoek et al. have shown, using a Ag₄ cluster, that the ethylene–oxygen interaction for the asymmetric geometry is about equal to that for the symmetric attack, from which it follows that the epoxide may be formed by both asymmetric and symmetric attack.³⁰ The oxygen–ethylene distance used in the latter investigation (1.60 Å) is very similar to the one that we used (1.55 Å). It should also be mentioned that **24** is very similar to the approach suggested for the oxygen transfer from oxo-iron porphyrin to ethylene based on a semiempirical MO/VB investigation.³⁶ We are now faced with a very serious problem: Does **24** lead to ethylene oxide, because it is more stable compared with **25**? To be able to answer this question, a very detailed calculation of the two transition states for the formation of ethylene oxide from **24** and **25** is necessary. Calculation of transition states for chemical reactions on a surface using extended Hückel calculations

is not feasible. We are thus left, as others who have been interested in the silver surface catalyzed epoxidation of ethylene,^{26,30} with the indications that the most stable silver-surface–oxygen–ethylene intermediate accounts for the experimental results.

Approach of ethylene to the terminal oxygen of the molecular on-top bound species in **10** produces a similar preference for the asymmetric intermediate with one of the ethylene carbons bound to the oxygen. The energetic and overlap population trends found for the interaction of ethylene with **10** are comparable to those found for the approaches shown in **24** and **25**.

One might ask here: Could oxygen transfer from some of the other molecular and atomic adsorbed oxygen species not be possible? Let us here try to discuss the likelihood of oxygen transfer from what we think are less realistic structures of molecular and atomic oxygen, in relation to oxygen transfer from an Ag(110) surface to ethylene.

Let us turn to the peroxy-like adsorbed molecule oxygen, **4**. It has been suggested for the analogous molecular peroxy complexes that the alkene has to approach the oxygen (which is going to be transferred to the alkene) along the oxygen–oxygen bond as shown in **26**.^{2e,37} The alkene can also approach perpendicular to the



metal peroxy plane.^{2e,36} It has been observed for instance that peroxy-titanium porphyrins are unreactive toward alkenes,³⁸ whereas titanium peroxide complexes in general are known to be good epoxidation species.^{2e,32} The reason for the unreactive peroxy-titanium porphyrin might be that the alkene cannot approach the peroxy bond as shown in **26**, because of steric repulsion between the alkene and the porphyrin ligand, whereas in the titanium peroxide complexes an approach of the alkene along the oxygen–oxygen bond is feasible. If molecular oxygen is present in the form of peroxy or bridging oxygen on a silver surface, the arguments outlined above might indicate that oxygen transfer from these species to ethylene is less probable, particularly when compared with the approach to atomic oxygen shown in **24**, because the approach of ethylene to the O–O bond as outlined in **26** will lead to steric repulsion between the silver surface and ethylene. We are thus left with the three atomic adsorbed oxygen types, **14**–**16**, and molecular oxygen, **10**. As the bridging atomic oxygen, **15**, has binding properties to the Ag(110) surface that are very similar to **13**, it might also be involved in oxygen transfer to ethylene in the same way as **13** although it is slightly more strongly bound to the surface than the on-top bound atomic oxygen, **13**. Calculations of the interaction between the oxygen in **15** and ethylene shows that an asymmetric approach of ethylene is most feasible. A bridging atomic oxygen on a silver surface has been used in previous studies of oxygen transfer to ethylene.^{26,30} The bridging atomic oxygen can also be a prestate for **13** as it very easily can be converted to **13** by a movement along the [110] axis. On the basis of our knowledge of molecular systems we do not think that **15** is the active oxygen species for epoxidation of ethylene, but we cannot of course exclude **15** as being present on the silver surface and active in the oxygen-transfer step. The two types of adsorbed oxygen **11** and **16** are interesting; in both cases the ethylene has to come very near to the surface to interact with these oxygens. This is probably unrealistic compared with the approach depicted in **24**, but as will be shown in the next section,

(37) (a) Finn, M. G.; Sharpless, K. B. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1986; Vol. 5, p 247. (b) Bach, R. D.; Wolber, G. J.; Coddens, B. A. *J. Am. Chem. Soc.* **1984**, *106*, 6098. (c) Jørgensen, K. A.; Hoffmann, R. *Acta Chem. Scand.* **1986**, *B40*, 411. (d) Jørgensen, K. A.; Wheeler, R. A.; Hoffmann, R. *J. Am. Chem. Soc.* **1987**, *109*, 3240.

(38) (a) Ledon, H. J.; Varescon, F. *Inorg. Chem.* **1984**, *23*, 2735. (b) Bortolini, O.; Di Furia; Modena, G. *J. Mol. Catal.* **1985**, *33*, 241.

(36) Servin, A.; Fontecave, M. *J. Am. Chem. Soc.* **1986**, *108*, 3266.

TABLE III: The Silver-Oxygen Overlap Populations for 13, 27, and 28

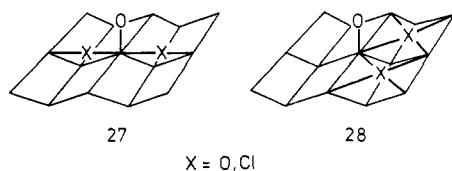
	Ag-O overlap population		Ag-O overlap population
13	0.280 ^a	28 (X = O)	0.276
27 (X = O)	0.261	28 (X = Cl)	0.259
27 (X = Cl)	0.222		

^aSilver-oxygen overlap population.

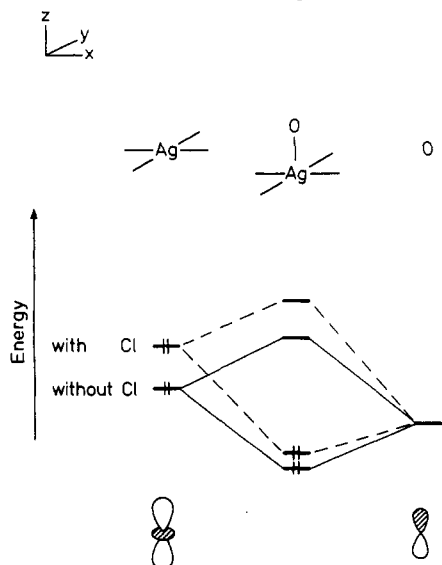
these adsorptions of oxygen (and chloride) in the grooves of the silver surface might account for the effect of moderators on the reaction course.

A Possible Model for the Effect of Moderators (Chlorine)

Chlorine has been found to increase the yield of ethylene oxide significantly (reduced combustion) when added as a moderator during the reaction.² It has also been shown on silver powders that only if the total amount of oxygen atoms adsorbed exceeds half the number of silver surface atoms (i.e., $\theta_0 > 0.5$) will the adsorbed oxygen be in a state able to react with ethylene to yield the epoxide. We have studied the effect of the presence of both oxygen and chlorine in the grooves of both **10** and **13**. Let us start with the influence of oxygen and chlorine in the grooves of Ag(110) when atomic oxygen is bound to the top of a silver atom. Two types of models have been considered, **27** and **28**. In **27** X (Cl



or O) is bridging between two silver atoms in two different rows, and in **28** X is placed over a silver atom in the second layer. Table III shows the change in silver-oxygen overlap with X as shown in **27** and **28**. It appears from the results that the presence of oxygen or chlorine in the grooves of the silver surface leads to a decrease of the Ag-O overlap population.³⁹ The largest decrease is found for chlorine placed as bridging between two silver atoms in two different rows, **27**. Our calculations indicate that the Ag-O bond is particularly weakened by the presence of chlorine in the grooves, which makes the oxygen transfer to ethylene easier. Chlorine and oxygen in the grooves push the d orbitals up in energy relative to the case where no moderator atoms are present. This is shown schematically for the d_{z^2} orbital of silver to the left in **29**. The interaction between the silver d_{z^2} orbital without chlorine



29

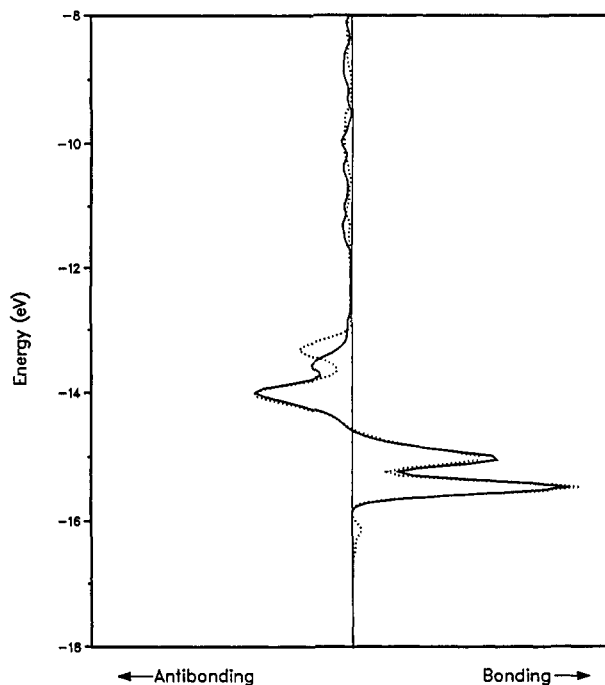


Figure 4. COOP curves for **13** (full line) and with chlorine as moderator, **27** (dotted line).

present and the oxygen p_z orbital is shown as the full line, and the interaction with chlorine present as the dotted line in **29**. It is seen that the bonding level is not perturbed significantly by the interaction, whereas the antibonding level is pushed up in energy when chlorine is present. Figure 4 shows a comparison of the COOP curves for **13** and **27** (X = Cl).

The increase in energy of the location of $\sigma^*_{\text{Ag-O}}$ in the presence of chlorine in grooves of the silver surface is easily seen from the dotted line in Figure 4. It appears that this level is pushed up to ~ -13.2 eV from ~ -13.7 eV in **13** (the full line).

We have done the same analysis for end-on adsorbed molecular oxygen, **10**, and also here we observe a decrease in Ag-O overlap population, but we see no difference in O-O bonding with or without chlorine. This indicates that the O-O bond in **10** is not activated by the presence of chlorine in the grooves.

With the model used here for the presence of chlorine as moderators in the silver surface catalyzed epoxidation of ethylene we are thus able to explain the effect of chlorine on the reaction course. However, one should be aware that it is a problem in analyzing the effect on the Ag-O bond as presented here, because probably anything attached to that Ag will weaken the Ag-O bond because it uses up some of its bonding capacity. Another view on the effect of chlorine has been put forward in the recent theoretical work by Carter and Goddard, who believe that it is the specific sites blocked by chlorine which increase the selectivity of the catalyst.²⁶

The halogens make the oxygen in **13** easier to transfer to an ethylene, whereas the oxygen that is going to be transferred in **10** is unaffected by the presence of chlorine. These results seem to favor **13** as the active intermediate in the epoxidation of ethylene catalyzed by a silver surface. It should also be mentioned that the presence of electron-withdrawing groups around the oxo-transition-metal function in the molecular systems increases the reactivity of the oxo-transition-metal complex.^{35,40}

It might be appropriate to finish this paper by a comparison to some recent experimental results.⁴¹ It has been found that silver complexes can catalyze the epoxidation of alkenes: AgNO_3 in the presence of pyridine and Ag_2O are able to mediate the epoxidation of different alkenes with iodosylbenzene as the oxygen donor. With *cis*-alkenes as the substrate *trans*-epoxides are the

(39) Similar arguments have been put forward by others; see ref 30.

(40) Nappa, M. J.; Tolman, C. A. *Inorg. Chem.* **1985**, *24*, 4711.

(41) Jørgensen, K. A.; Larsen, E. *J. Chem. Soc., Dalton Trans.*, in press.

TABLE IV: Extended Hückel Parameters

orbital	H_{ii} , eV	ζ_1^a	ζ_2^a
H(1s)	-13.60	1.30	
C(1s)	-21.40	1.625	
C(2p)	-11.40	1.625	
O(2s)	-32.30	2.275	
O(2p)	-14.80	2.275	
Ag(5s)	-11.10	2.244	
Ag(5p)	-5.80	2.202	
Ag(4d)	-14.50	6.070 (0.559 10)	2.6630 (0.604 76)

^a Exponents and coefficients in a double- ζ expansion of the metal d orbitals.

major product. The presence of pyridine with an electron-withdrawing group in the para position leads to a more effective catalyst when AgNO₃ is applied compared with, e.g., the presence of pyridine, and isotopic labeling experiments as well as Ag₂O₂-mediated epoxidations could be indications for an intermediate that is comparable to 13. These results might thus build a bridge between the epoxidations catalyzed by a surface and those catalyzed by metal complexes.

Summary

The present study indicates that three different types of adsorbed molecular oxygen on Ag(110) are preferred. These are end-on adsorption on top of a silver atom on the surface and bridging between two silver atoms in the [110] or [001] direction. Molecular oxygen adsorbed as peroxo-like on top of a silver atom on the surface or located along the [110] direction in the grooves seems to be slightly less favorable. However, the present type of calculations does not give a clear-cut picture of the most probable type of adsorbed molecular oxygen. Atomic oxygen appears to have a preference for being adsorbed either on top of a silver atom on the surface or between two silver atoms in the [110] direction. Atomic oxygen located in the grooves of the surface is also possible. The adsorption of molecular oxygen to the silver surface leads to population of the π^*_{O-O} orbitals as well as in some cases the

antibonding orbitals between silver and oxygen. It is suggested that an oxo-silver species is probably the one which leads to epoxidation of ethylene. The ethylene can approach the oxygen in the oxo-silver species in two different ways, an unsymmetric way in which the oxygen interacts with one of the carbons in ethylene or a symmetric interaction where the oxygen interacts with both carbons. Our calculations prefer for the former. Such an interaction opens up the possibility for free rotation around the carbon-carbon bond in ethylene, leading to a nonstereospecific oxygen-transfer step. This is in accordance with the experimental results. The transfer of oxygen from several of the other molecular and atomically adsorbed oxygen species to ethylene is also discussed. The increased yield of ethylene oxide (reduced combustion) when chlorine is present during the reaction has been suggested to be caused by adsorption of chlorine in the grooves of the silver surface leading to a decrease in the overlap population between silver and oxygen, making the oxygen easier to transfer to ethylene.

Acknowledgment. Thanks are expressed to The Danish Natural Science Research Council and Thanks to Scandinavia, Inc. (especially Mr. Richard Netter) for financial support. Valuable comments by Professor Robert J. Madix and Marja Zonneville are also acknowledged. Professor R. A. van Santen is acknowledged for sending results prior to publication. Thanks are also expressed to Hanne Kirkegaard for the word processing and to Arne Lindahl for the draftwork.

Appendix

All the calculations have been performed using the extended Hückel method.^{23a} The parameters are listed in Table IV. In all the calculations the following bond distances (Å) were used: Ag-Ag(110), 2.89; Ag-O, 2.12; O-O, 1.40; C-C, 1.36; C-H, 1.08. All surface calculations were of the tight-binding extended Hückel type.²³ In all cases nine k points were used in the irreducible part of the Brillouin zone.

Registry No. Ag, 7440-22-4; O₂, 7782-44-7; atomic oxygen, 17778-80-2; ethylene, 74-85-1; ethylene oxide, 75-21-8; chlorine, 7782-50-5.

Coadsorption and Reaction of Water and Potassium on Ag(111)

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KOH formation on Ag(111) has been studied with UPS, XPS, TPD, AES, isotopic exchange, and work function measurements. O(1s) XPS indicates that coadsorbed potassium and water react very slowly at 100 K at submonolayer and multilayer K precoverages. D₂ and D₂O TPD spectra of K + D₂O layers provide evidence for KOD formation and decomposition temperatures, as well as the desorption temperatures of water that hydrates KOD. UPS, XPS, and TPD indicate that KOD formation is complete at 300 K. In TPD of H₂O on KOD, D-for-H exchange is observed. KOH layers are altered by exposure to a 3-keV electron beam.

I. Introduction

Alkali-metal atoms present in small amounts produce marked promotional effects in heterogeneous catalysis. These effects have motivated numerous studies of alkali-metal coadsorption systems, which have been recently reviewed.¹ Under typical catalytic conditions, the alkali-metal atoms are present as cations of an ionic salt rather than as a simple metal. Though often neglected, the counterions may play a role in catalytic promotion or selectivity either by competing with other substrate/adsorbate species for electron density from the alkali, or by direct participation in the

catalytic reactions. Thus, model studies of the promotional effects of alkali metals will be aided by methods for the routine in situ preparation of alkali-metal salt layers under ultra-high-vacuum (UHV) conditions. The UHV preparation of KOH is a priori among the simplest of these, requiring only a simple reaction between H₂O and K. From KOH, a UHV synthesis of adsorbed carbonate is then realizable by its reaction with CO₂ at room temperature.² Hydroxides and carbonates are most often cited

* Corresponding author.

(1) Bonzel, H. P. *Surf. Sci. Rep.* **1987**, 8, 43.
(2) Blass, P. M.; Zhou, X.-L.; White, J. M. *J. Vac. Sci. Technol.* **1989**, A7, 2009.