molecule 1, the cytosine is involved in Watson–Crick base pairing with a second dimer (1,2) (see Figure 1). In addition the cytosine bases of molecule 2 are strongly stacked, as schematically depicted in Figure 3. Finally, stacking occurs between the cytidine base of molecule 2 and the G(1) of a neighbouring molecule 2 (not shown).

In summary, it is concluded that the GG part of the described structure appears to be similar to the structure found in the crystal structure[16] of *cis*-Pt(NH$_3$)$_2$–(pGpG). As a result of intermolecular interactions of the cytosines, the conformation of this nucleobase in the structure—especially with respect to its stacking on the central guanine—does not reflect the conformation of the compound in solution.

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Registry No. *cis*-Pt(NH$_3$)$_2$[d(CpGpG)-*N*7(2),*N*7(3)], 105834-59-1.

Supplementary Material Available: Tables with conformational parameters of the CpGpG units in each of the three molecules in solid *cis*-Pt(NH$_3$)$_2$[(CpGpG)-*N*7(2),*N*7(2),*N*7(3)] and atomic coordinates with *B* values (5 pages). Ordering information is given on any current masthead page.

How Does Prereduction Affect Electronically the Catalytic Properties of MoO$_3$ toward Olefin Oxidation

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The recent observation[1] that the (100) face of MoO$_3$ can catalytically convert propylene into acrolein is of much interest and may be used as a model to understand the catalytic properties of bismuth molybdates.[2] To explain the olefin adsorption, the existence of an "open" Mo atom on the surface, hence prereduction, was suggested. Consequently, not all the Mo atoms[3] can be d^0 (in a +6 oxidation state), a fact in sharp contrast with the assumption[4] of an empty d band in bismuth molybdate catalysts.

To probe the electronic implications of this prereduction step, band structure calculations[5] were carried out on both naked MoO$_3$ and the whole surface/olefin system. The analysis shows that (i) the surface acquires a metallic character which enhances its ability to chemisorb the olefin and (ii) the extra electron density is *not* localized on the open metallic site but in bulk like states. This "reservoir" is emptied upon adsorption, thereby filling a new set of surface/adsorbate bonding states which fall *below* the Fermi level. A stronger chemisorption results.

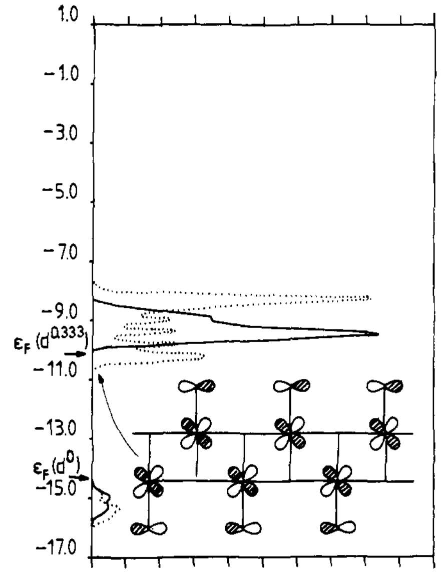
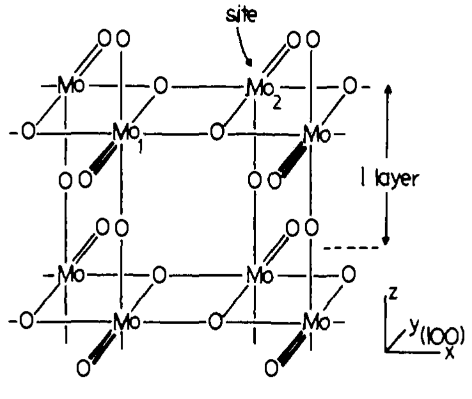


Figure 1. Projected density of states (DOS) of *xy* (dotted line) and *yz*/*xz* (solid line) of the Mo atoms in the surface **1**; the labels ϵ_F (d^0) and ϵ_F (d$^{0+0.333}$) refer to the Fermi level for various electron counts. The topology of the *xy* band at the Γ point is also indicated, from a top view.

The (100) face of MoO$_3$, perpendicular to the natural cleavage plane of layered[7] MoO$_3$, has never been structurally characterized. The calculations were performed on a three-layer ribbon with two Mo atoms in the outermost layer belonging to the unit cell;[8] in this model,[12] one (Mo$_1$) retains the apical oxygen away from the bulk while the other (Mo$_2$)—the site—is opened, as shown in **1**.



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(8) With each Mo in a local O$_h$ geometry and all Mo–O distances set at 1.98 Å, the band gap and overlap populations obtained[9] for bulk MoO$_3$ agree well with the experimental[10] and theoretical[11] data.

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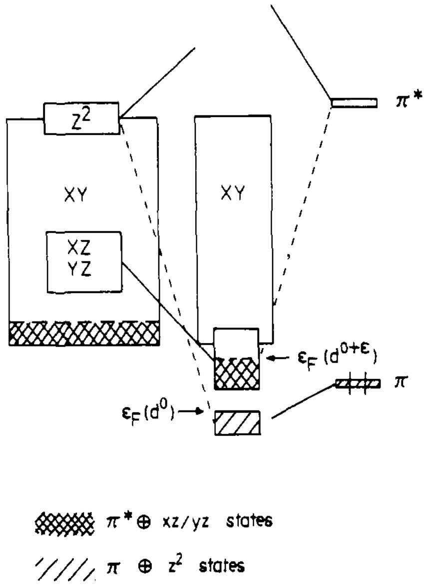
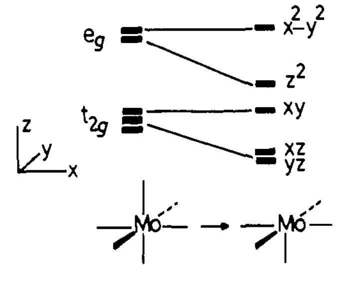


Figure 2. Schematic interaction diagram between the surface and the propene adsorbate, see text. The circled "plus" means "bonding".

Reduction of the surface, i.e., populating its d band, does not localize the electrons in the Mo_2 *xz* and *yz* π-type of hybrids despite the removal of an apical π-donor, see **2**. Rather, the *xy* states displaying Mo–Mo σ overlap parallel to the surface develops into a band wide enough for its bottom to lie below the protruding *xz*/*yz* hybrids and house the extra electron density. Figure 1 illustrates this point.



2

Sticking a propene above Mo_2 turns on a σ donation from π into z^2 as noted[4] by Anderson. However, bonding states are also generated between empty *xz*/*yz* of Mo_2 and π^* of C_2H_4. These states, empty in an overall d^0 surface, emerge below[13] the bottom of *xy* not involved in the adsorption and get filled by electron transfer in the reduced system. Figure 2 describes schematically this mechanism and is based on a DOS analysis of the overall system. Numerically the reduction process was simulated by injecting[14] one or two electrons in the unit cell starting from a d^0 system. With ϵ representing the averaged[15] extra electron population and Δ the variation of electron population between after and before adsorption, we have for $\epsilon = 0.333$, $\Delta(xy) = -0.324$, $\Delta(xz/yz) = +0.994$, $\Delta(z^2) = +0.138$, $\Delta(\pi) = -0.15$, and $\Delta(\pi^*) = +0.45$. Prereduction strengthens the C_2H_4/MoO_3 bonding; the averaged Mo–C overlap population goes from 0.10 ($\epsilon = 0$) to 0.25 ($\epsilon = 0.333$). The surface *xy* states act as a "reservoir", temporarily storing the electron density that it eventually pours into new surface/adsorbate bonding levels.[16] These electronic factors may constitute the *raison d'être* of the prereduction. These conclusions are drawn out of semiquantitative computations; further insight could be gained from more sophisticated calculations and perhaps by an experimental study of the catalytic properties of doped MoO_3.[17] Yet, our complementary calculations[9] on the (100) MoO_3/propene system point out that prereduction plays a crucial role in the rate-determining step, the first C–H scission, toward acrolein formation. This finding may be supported by infrared and ESR measurements showing[18] that the Mo atoms are reduced in the catalytic cycle with the $Bi_2Mo_3O_{12}$ system.

Acknowledgment. Thanks are due to E. Vignon for the typing and CIRCE for technical assistance.

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[13] With a chemically reasonable Mo–C distance of 2.1 Å.

[14] The amount of electron density referred to is small enough to justify the rigid band model.

[15] $\epsilon = 0.3333$ means formally one d^4 Mo and five d^0 Mo per cell.

[16] A somewhat similar effect was described in: Silvestre, J.; Hoffmann, R. *Langmuir* **1985**, *1*, 621.

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ESR Studies on the Radical Cation Mechanism of the Ring Opening of Cyclopropylamines

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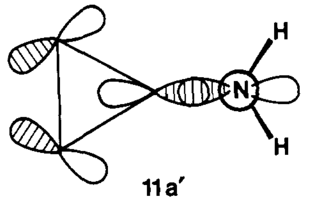
Cyclopropylamine radical cations have been implicated in the mechanism of inactivation of monoamine oxidase and cytochrome P-450 by cyclopropylamines.[1,2] The key step in the proposed mechanism is illustrated for the parent compound in Scheme I and consists of the ring opening of the aminium radical cation **1** to the carbon-centered radical **2** which subsequently attacks the active site of the enzyme.[2] Here we present ESR evidence for this ring-opening reaction and report that **2** is not converted to the nitrogen-centered radical **3** whereas the corresponding reaction for the neutral radical (**5** → **6** in Scheme II) proceeds to completion at similar temperatures. These results provide a firm basis for the radical cation mechanism of enzyme inactivation,[1,2] in keeping with the structural evidence that the inactivator is bound to the enzyme through carbon rather than nitrogen.[2]

The radical cation from cyclopropylamine was generated radiolytically in several Freon matrices,[3] $CFCl_3$ and CF_3CCl_3 being the most suitable for the study of the sequestered radical cation. Figure 1 shows the ESR spectrum of the ring-opened radical cation **2**,[4] the β-hydrogen hyperfine couplings differing significantly from those for neutral $CH_2CH_2CH{=}NR$ radicals[5] (Table I). The formation of **2** from **1** can be rationalized by considering the HOMO of cyclopropylamine,[6] the removal of an electron from this 11a′ orbital leading to a weakening of the C–C bonds. That



11a′

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[3] For experimental details, see, e.g.: Snow, L. D.; Williams, F. *Faraday Discuss. Chem. Soc.* **1984**, *78*, 57.

[4] **2** is a distonic radical cation. For other examples, see: (a) Yates, B. F.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1984**, *106*, 5805. (b) Sack, T. M.; Cerny, R. L.; Gross, M. L. *J. Am. Chem. Soc.* **1985**, *107*, 4562.

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