

EXTENDED HÜCKEL CALCULATIONS ON THE SURFACE COMPLEXES  
OF PROPYLENE WITH A CUPROUS OXIDE FRAGMENT

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Extended Hückel calculations have been performed on a number of  $C_3H_6$  complexes with a linear O—Cu—O fragment. The influence of the mutual orientation of  $C_3H_6$  and the  $Cu_2O$  fragment in hypothetical surface complexes upon the energy of the system and electron density distribution has been determined. The role of these complexes in catalysis is discussed.

Расширенным методом Хюккеля проведен расчет ряда гипотетических комплексов  $C_3H_6$  с линейным фрагментом структуры закиси меди O—Cu—O. Найдено влияние взаимной ориентации  $C_3H_6$  и фрагмента  $Cu_2O$  в гипотетических поверхностных комплексах на энергию системы и распределение электронной плотности в ней. Обсуждается роль этих комплексов в катализе.

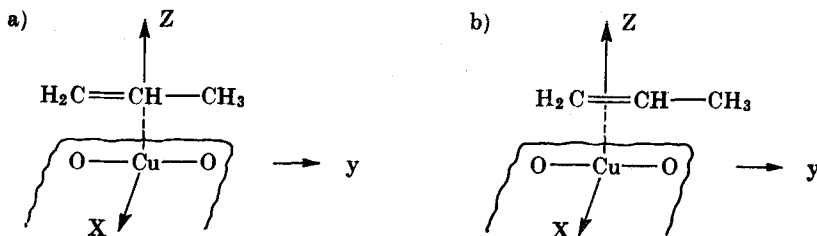
The oxidation of propylene to acrolein over oxide catalysts is known to occur via hydrogen atom abstraction from the methyl group and the formation of an allylic type intermediate surface compound oxidizable to the final product /1-3/. The first step in this process is likely to be the formation of a surface complex involving the reagents and the catalyst /4, 5/. One may assume that a  $C_3H_6$  molecule in a given complex has already undergone those changes which are necessary for allyl oxidation, i. e. decrease of the C=C and C—H (in the  $CH_3$  group) bond strengths

and increase of the C—C bond strength. Literature data partly support this view /6, 7/ but give no satisfactory information on the nature of these complexes.

The purpose of this work was to determine the energy of formation of surface complexes of propylene with a linear O—Cu—O fragment for different orientations of adsorbent and adsorbate and to find the electron density distribution in the system under study by the extended Hückel method /8/, using the same program as in Ref. /9/.

When choosing a  $\text{Cu}_2\text{O}$  crystal model /10/, we have taken into account that the linear O—Cu—O fragment lies in the (110) plane, which has the higher reticular density and apparently emerges to the surface. The geometry of the  $\text{C}_3\text{H}_6$  molecule was taken from Ref. /11/.

We have calculated two types of hypothetical surface complexes corresponding to arrangements (a) and (b) of propylene, for both the parallel and perpendicular



orientation of the  $\text{C}_3\text{H}_6$  plane relative to the surface fragment. Each arrangement was considered at angles  $0^\circ$ ,  $45^\circ$ ,  $90^\circ$  and  $135^\circ$  formed by the C=C bond and the Y axis; the double bond was always perpendicular to the Z axis. The Cu—C distance was chosen to be equal to the sum of the covalent radius of carbon in a single bond,  $r_{\text{C}-\text{C}} = 0.77 \text{ \AA}$ , and the radius of copper in the  $\text{Cu}_2\text{O}$  structure estimated according

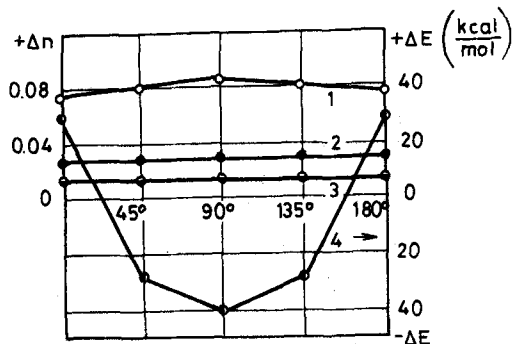


Fig. 1. Population of the C=C (1), C-C (2) and C-H (3) bonds and the total energy of the system (4) for adsorption form (a), for various positions of  $C_3H_6$  in the plane perpendicular to the surface

to Ref. /12/,  $r_{Cu^+} = 1.05 \text{ \AA}$ . The ionization potentials of the 4s, 4p and 3d orbitals for the configurations of the Cu atom in the ground state were calculated according to Ref. /13/, using spectral data /14/ and found to be  $-7.72$ ,  $-3.73$  and  $-10.44$  eV, respectively. The ionization potentials used for the oxygen, carbon and hydrogen atoms were:  $I(O2s) = -28.46$ ,  $I(O2p) = -13.61$ ,  $I(C2s) = -16.59$ ,  $I(C2p) = -11.26$ ,  $I(H1s) = -13.60$  eV, as in Ref. /14/. The resonance integrals were determined from the Wolfsberg-Helmholz equation (15), with a K value of 1.75. The Slater exponents were obtained according to the rules formulated in Ref. /16/.

The calculated energies of the isolated  $C_3H_6$  and the fragment are:

$E_{C_3H_6} = -282.89$  and  $E_{CuO_2} = -350.89$  eV, the population of n bonds in  $C_3H_6$  were found to be  $n_{C=C} = 1.276$ ,  $n_{C-C} = 0.777$  and  $n_{C-H} = 0.795$ .

Figure 1 shows the change in the energy of the system ( $\Delta E$ ) relative to the total energy of the isolated components and the variation of the C=C, C-C and C-H (in  $CH_3$  group) bond populations against the angle between the C=C and

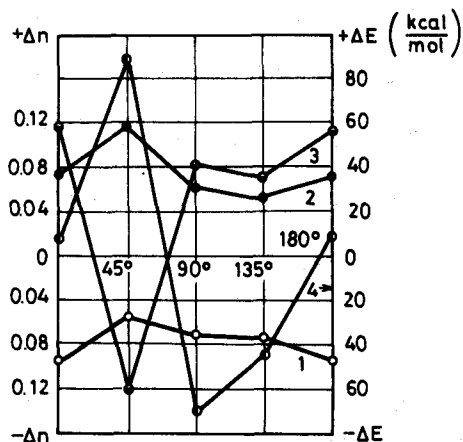


Fig. 2. Same as in Fig. 1, for a parallel orientation of the planes

O—Cu—O bonds, for a perpendicular arrangement of the C=C—C plane and that of the surface fragment, and for arrangement (a) of the olefin.

At angles 45, 90 and 135° between the C=C and O—Cu—O bonds, the energy of the system decreases, i. e. the complexes formed are energetically favourable both for the decomposition and formation of acrolein. An analogous picture is observed in the case of arrangement (b). We assume that such complexes are catalytically inactive.

Upon the rotation of the  $C_3H_6$  molecule in the plane parallel to the surface, a different situation is observed. For arrangement (a) of  $C_3H_6$  (Fig. 2), the maximum decrease in the energy of the system is reached when the angle between the C=C and O—Cu—O bonds is 135°. For arrangement (b) (Fig. 3), the orientation of the C=C bond with respect to the O—Cu—O fragment is energetically the most favourable at 90 and 135°. In contrast, if the double bond is at an angle of 45°, both forms are energetically unfavourable (the energy of the system increases). In this

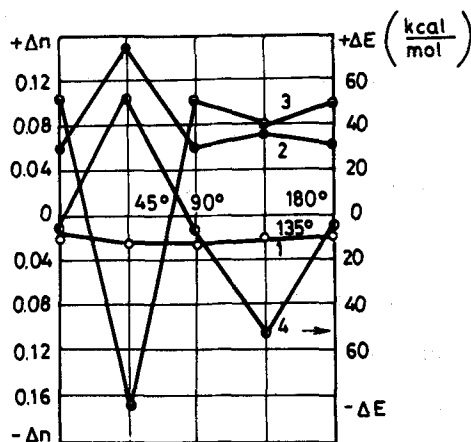


Fig.3. Same as in Fig. 1, for form (b) and a parallel orientation of the planes.

case, a decrease in the population of the C=C bond and an increase in those of the C-C and C-H bonds are characteristic of all orientations. Except for complexes with angles of  $45^\circ$  between the C=C and O-Cu-O bonds, in which the population of the C-H bond drops sharply, the positive charge on the hydrogen atom increases ( $\Delta q = 0.30$ ) and a new H-O bond with a population of  $n = 0.30$  is formed. Thus, if the planes of the C=C-C bond and the surface fragment are parallel to each other, the energetically favourable complexes are characterized by a decreased C=C bond strength and by increased C-C and C-H bonds strengths, while the energetically unfavourable complexes by decreased C=C and C-H bond strengths and an increased C-C bond strength. The former seem to be inactive in the formation of acrolein. The oxidation of propylene to this product may, in our opinion, occur via energetically unfavourable complexes in which the C=C bond is oriented to O-Cu-O at the optimum angle, i. e.  $45^\circ$  in our calculations. It is in these complexes, both in forms

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(a) and (b), that the populations of the bonds under consideration change in the direction favourable for hydrogen abstraction and the formation of an intermediate allyl compound. The formation of such complexes requires some additional energy which may be supplied, for instance, by heating the reaction mixture. We believe that propylene is adsorbed to give the optimum angle between the C=C and O—Cu—O bonds. The same result in energetically favourable but catalytically inactive complexes may be obtained by rotating the  $C_3H_6$  molecule into a position favourable for acrolein formation.

The cases discussed do not include all the theoretically possible  $C_3H_6$  complexes involving a surface fragment. However, the data obtained point to an important influence of the mutual orientation of an olefin molecule and a catalyst fragment on the energy of the system and the electron density distribution.

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