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


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Received August 1, 1974

Extended Hückel calculations have been performed on a number of C\textsubscript{3}H\textsubscript{6} complexes with a linear O--Cu--O fragment. The influence of the mutual orientation of C\textsubscript{3}H\textsubscript{6} and the Cu\textsubscript{2}O fragment in hypothetic surface complexes upon the energy of the system and electron density distribution has been determined. The role of these complexes in catalysis is discussed.

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\textsubscript{3}H\textsubscript{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\textsubscript{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 Cu$_2$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 C$_3$H$_6$ molecule was taken from Ref. /11/.

We have calculated two types of hypothetic surface complexes corresponding to arrangements (a) and (b) of propylene, for both the parallel and perpendicular orientation of the C$_3$H$_6$ plane relative to the surface fragment. Each arrangement was considered at angles 0, 45, 90 and 135° 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, 

\[ r_{C—C} = 0.77 \text{ Å}, \] and the radius of copper in the Cu$_2$O structure estimated according to