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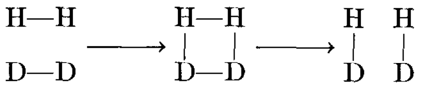
LETTERS TO THE EDITORS

Conservation of Orbital Symmetry and the Crystal-Field Surface Orbital–Bond Energy Bond Order (CFSO–BEBO) Method

Recently, Knor (1) critically reviewed the crystal-field surface orbital–bond energy bond order (CFSO-BEBO) method of Weinberg *et al.* (2, 3) that has been employed to calculate empirically the potential energy along the reaction coordinate for various surface-adsorption and catalytic processes. He mentioned several limitations of the method, including the necessary assumptions of localized surface orbitals and their occupations, the validity of the extension of BEBO correlation in gas molecules to surface molecules, the *a priori* postulation of nuclear positions along the reaction coordinate, and the assumed equal partition of electrons from the bonds that are broken to the bonds that are formed.

Inspite of these limitations, the CFSO–BEBO method gives reasonable estimates of the energetics of several surface processes (2). The recent application of the method to the reactions of $CO + O_2$, $NO + CO$, and $H_2 + O_2$ on Pt to distinguish the feasibility of the Rideal–Eley and the Langmuir–Hinshelwood mechanisms by comparing the calculated activation energies involved prompted us to write this note to discuss another limitation of the method; namely, the method does not consider the conservation of electron orbital symmetry (4, 5) and nuclear symmetry (6) along the reaction coordinate. Because of the assumptions involved, the BEBO method is in fact a ground-state calculation of the relative stabilities of the quasimolecules along the reaction coordinate. Consideration is not given to the possible existence of an energy barrier to the proposed direction of electron flow due to poor net overlap of the orbitals involved. If one considers a small segment of the reaction pathway (i.e., a small but discrete change in the set of nuclear positions) as a chemical reaction, the BEBO method gives the heat of the reaction and not the activation energy of the reaction, unless the two happen to be the same. *Thus, the activation energy estimated by the method is the lowest possible for that assumed set of nuclear movement and can be much lower than the real value if the assumed mechanism is symmetry forbidden.*

As an example of the neglect of orbital symmetry in the BEBO method, consider the mechanism that involves a four-center transition state for the H_2–D_2 exchange reaction.



This mechanism is symmetry forbidden and would have very high activation energy, because, according to Woodward and Hoffman (4), the orbitals of the ground-state reactant and ground-state product do not correlate. Equivalently, according to Pearson (5), there is lack of net positive overlap of the highest occupied orbitals with the lowest unoccupied orbitals of the molecules involved. However, neglecting

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the isotope effect, the activation energy is calculated to be zero by the BEBO method.

The BEBO method was originally used by Johnston (*7*) to estimate the activation energy of reactions involving the transfer of hydrogen atoms. Since the 1s orbital of H is spherical, such reactions are usually symmetry allowed (*5*). Orbital symmetry, however, becomes much more important in determining the feasibility of a reaction mechanism involving electrons in nonspherical orbitals, such as the p, d, π, and δ orbitals. This would include most reactions involving molecules of more than one atom. In fact, the importance of symmetry in heterogeneous catalysis has been recognized. In the conceptual models of Wolfram and Morin (*8*) and Mango (*9*) for catalytic reactions, the magnitude of the activation energy is shown to depend on the availability of orbitals of correct symmetry, occupation, and relative energies for both the molecular and surface orbitals.

The presence of a high density of orbitals of different symmetries near the Fermi edge of *d*-band metals (*10, 11*) makes the adsorption of molecules on these metals not very dependent on the restrictions imposed by the symmetry rules. These restrictions, however, could be very important in reactions between adsorbed molecules, or between a gas-phase molecule and an adsorbed molecule. This is because, although adsorption results in mixing of some molecular orbitals with surface orbitals, most molecular orbitals are largely preserved. This has been observed for adsorption of small molecules on Ni, Pd, Pt (*12–14*), and ZnO (*15*). Therefore, electron flow between orbitals of such adsorbed molecules could depend as critically on the symmetry rules as the gas-phase reactions. Thus, symmetry consideration that is ignored in the BEBO method should be made in any complete analysis of a reaction mechanism.

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