LETTER TO THE EDITOR

Reply to Comments on the CFSO BEBO Approach, *Journal of Catalysis* 47, 140 (1977)

The CFSO BEBO method which we have used in describing the interaction energies of adsorbed species on metal surfaces cannot be derived from theory. It is in its entirety an empirical model based heavily upon chemical intuition and an extension of the gas phase BEBO model to situations far more complex than the simple hydrogen transfer reactions (1) for which the method was originally contrived. While there is some theoretical justification for the BEBO method for these hydrogen transfer reactions, none exists for its use in chemisorption on metal surfaces. It is, rather, a totally empirical calculation using parameters taken largely from bulk compounds and gas phase spectra of atomic and molecular species. Its utility lies solely in the fact that, for the cases tested so far, the method has succeeded in predicting a great deal of the empirical details of the energetics of the chemisorption of simple gases on transition metal surfaces. While it might have been expected that these calculations would represent these systems qualitatively, the nearly quantitative agreement between the method and most of the calculated energies is surprising, indeed. It has been this remarkable quantitative success with simple systems like hydrogen on platinum (2) that has provided the impetus to investigate the method for more complex systems (3).

In presenting these results we have tried to make it clear wherever it seemed appropriate how the calculational procedures of the model might be related to more fundamental properties of the systems examined. While some of these connections may have seemed somewhat speculative, they have been preferred in the hope of making the calculations more plausible.

Knor's criticisms of the calculations appear to us to be directed toward a more literal view of some of these rationalizations than we intended and to some extent seem to be derived from a lack of perception of some of the more important details of the calculational procedures.

The "crystal field" name for this model is designed to focus attention on the assumed role of the bulk crystal structure in determining the spatial configurations of the relevant d orbitals at the surface. The probable effects of the lack of bulk symmetry introduced by the presence of the surface are discussed in Ref. (2). The concept of a partially occupied surface orbital is consistent with the local (surface) density of states (proportional to the imaginary part of the surface Green's function for the crystal). That it is substantially more narrow than the bulk density of states is a generally accepted notion (4, 5), one which has been confirmed experimentally using ultraviolet photoelectron spectroscopy. Knor himself admits to such empirical evidence for localized binding [his references (13–16)].

The bond energy–bond length correlations for gas phase hydrogen is not, as Knor suggests, based on only three points. In fact a multiplicity of excited states have

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been used with the ground state and the gas phase Lennard–Jones parameters to deduce the BEBO correlation for this molecule. The fact that the method succeeds as well as it does for hydrogen transfer reactions suggests that the *gas phase* BEBO correlation is probably a valid one.

The empirical optimization scheme suggested by Knor in his paragraph iv is carried out within the context of the model in its present form by maximizing the orbital overlap between the adsorbate and the crystal field orbitals of the surface atom.

The so-called "postulated mechanisms" are a result of conservation of bond order, which is a basic postulate of the model. The specific "geometric arrangement" was only important in the case of the small adsorbate, hydrogen. Some chemical intuition is employed in our prescription of the bonds being "broken" and those being "formed," but this simply represents a reasonable qualitative description of the chemisorption event. Whether or not the enterprise is energetically favorable is a result of the calculation.

Our reasons for using 43.6 kcal/mol for the Pt–Pt single bond energy are clearly outlined in our publications. The difference between this value and that of Higuchi *et al.* (*6*), 23 kcal/mol, lies in Brewer's (*7*) recognition that single bond energies should be related to the differences between the energy of the metal atom in the crystalline solid and excited state with the same electronic configuration, rather than the difference between the atom in the crystalline solid and the *ground state* gas atom. The formulation of Higuchi *et al.* is so oversimplified that it cannot seriously be considered to be more than an alternative empirical calculation whose parameters have been adjusted to give consistent results. It has been successful only because they used Pauling's scale of electronegativities, which is based upon the same assumption they used for the single bond energies for metal–metal bonds (an assump-

tion which diverges from the Brewer model which we have used) and empirical bond energies for the Group VIII hydrides.

The increase in the Pt–H bond length upon complete H–H dissociation is a detail which is unimportant to the primary conception of the model. It was introduced simply to maximize the overlap of the relatively small hydrogen atom with the protruding d orbitals of the surface and does, as Knor hints, represent multiple bonding with three surface atoms. The "reality" of such a detail should not be taken too seriously, as it is not a direct result of the fundamental assumptions of the model.

While we could have chosen to use arithmetic mixing rules for the single bond energies, it would have been necessary to introduce some empirical correction factor (like the Wolfsburg–Helmholz formula used in extended Huckel M.O. theory) in order to produce good results. We found that the geometrical mixing rules worked best, and they have a much firmer basis in fact for induced-dipolar interactions than arithmetic mixing rules. Since our methods envision a continuous BEBO correlation out to bond distances characteristic of gas–gas physical interactions, the use of geometric mixing rules avoids bothersome matching conditions for very weak bonds.

In trying to establish the Pt–C single bond energy, we have used alternate methods of calculation. None is based on the arithmetic mixing rules. The fact that we have used an "average" is related to our admission of ignorance of what the value should be and not to any assertion that the specific average selected is a correct one.

The "shapes" of the potential energy curves are not correct and we have never suggested that they are. Of course, energy versus bond order is *not* the same as energy versus bond distance and such curves will never approximate even *qualitatively* the more familiar *E* vs *r* curves. For cases where we have been able to transform the

calculation from bond order to bond distance, the force constants have not been good representations of what might have been expected. The only cases where we have advanced predictions about force constants have been for undissociated diatomic ad-species. The force constants have been for vibrations of the undissociated bonds, and they have been deduced from the *gas phase* correlations of bond order with force constant, not from the shape of potential energy curves relating energy with molecule–surface distance. The model is just too crude to give such results.

Our so-called "discontinuous combinations of intervals . . ." result from the continuous application of conservation of bond order which is one of the basic postulates of our model. In fact it is not true that all the adsorption minima occur at such points, e.g., carbon monoxide and nitric oxide minima occur quite naturally as a result of the shape of the gas phase BEBO curves. It is true that all gas–surface BEBO relationships are assumed to be linear and this is certainly suspect, especially when the bond order between the adsorbed molecule and a single surface atom is greater than unity. This happens rarely, however, and it seemed best not to introduce any additional adjustable parameters to account for nonlinearity in these BEBO correlations.

Finally, it is really difficult to say how seriously one should accept all of the details of the CFSO BEBO model. Its success has served, however, to emphasize the feasibility of the surface molecule concept of chemisorption on metals and, we think therefore, has been stimulating to those interested in the developing theory of chemisorption. It may remain for some time a useful and viable technique to probe the gross features of rather complicated adsorbate systems. The calculations are so simple and inexpensive compared to any acceptable "theory of chemisorption" currently available that they are instructive to perform on systems under study either theoretically or experimentally. It is important, however, to recognize the completely empirical nature of the procedure and not to be disappointed at the many interesting and important characteristics of adsorption and chemical reactions at surfaces which the method cannot predict a priori.

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