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## References and Notes

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# Potential Energy Barriers for Halogen Six-Center Reactions: Semiempirical Valence-Bond Predictions[1a]

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**Abstract:** An approximate, semiempirical valence-bond formulation is employed to compute potential energy surface reaction barriers for six-center reactions involving the halogens ($F_6$, $Cl_6$, $Br_6$, $I_6$) and hydrogen ($H_6$). The method is based on approximations comparable to those in the London-Eyring-Polanyi-Sato (LEPS) formulation. The surfaces are not adjusted using data for the systems treated, but are computed using parameter values that have been used in studies of other systems. The predicted energy barriers are in qualitative accord with existing experimental results for related systems.

The London-Eyring-Polanyi-Sato[2] (LEPS) semiempirical potential energy surfaces in many variations have been widely used in quasiclassical trajectory calculations. While the theoretical basis for these surfaces is rather weak, it seems to be a well-established fact that given reasonable adjustments of parameters the surfaces are realistic and accurate descriptions of the forces in at least certain types of chemical reactions.[3]

We have made many applications of one particular semiempirical valence-bond formulation to describe three- and four-atom systems.[4] In this method, first used by Raff, Stivers, Porter, Thompson, and Sims[5] to describe the $H_2I_2$ reaction system, the empirical adjustments are made using parameters that are specific to the types of atoms, rather than atom pairs. A well-studied reaction is used to adjust these parameters; for example, the measured activation energy for $H_2 + Cl \rightarrow HCl + H$ was used to obtain a value for the chlorine atom parameter.[6] In applications, we assume that the value of this parameter is independent of the environment of the particular atom; that is, the surface parameters are assumed to be transferable. The qualitative validity of this assumption is supported by the close accord between computed and experimental results for a number of systems. Here we make the assumption again and apply the method to six-center reactions.

Wright,[7] in 1970, suggested that a six-center transition state might offer a lower energy pathway for $H_2$, $D_2$ exchange than the four-center transition state. Recently, Dixon, Stevens, and Herschbach[8] have carried out SCF-CI calculations and obtained a barrier height of ~68 kcal/mol for $H_6$.

Shock tube[9] and stimulated Raman[11] experiments on the $H_2 + D_2$ exchange reaction have been interpreted in terms of a four-center process with an activation energy of 42 kcal/mol. Quantum-mechanical calculations[12-17] suggest an even higher barrier (as much as three times) than has been determined from these experiments. Quasiclassical trajectory studies[18,19] on various potential energy surfaces have failed to resolve the controversy surrounding the $H_2 + D_2$ reaction. Nevertheless, it seems to be a fact that the energy barrier to exchange is relatively high.

Other aspects of four-center reactions, in some respects related to the high energy barriers, are the collisional constraints, dynamic and steric, that affect the crossing from reactants to products. The trajectory results of Brown and Silver[19] illustrate the molecular orientational constraints on reaction in $H_2 + D_2 \rightarrow 2HD$. The trajectory studies of $H_2 + 2I$ by Raff, Thompson, Sims, and Porter[20] show the dynamics restrictions on four-center, termolecular processes. Thompson and McLaughlin[21] have investigated the severe constraints present in $H_2 + F_2 \rightarrow H + HF + F$ for reaction path geometries and reactant energy partitioning.

The inference from all these studies, and others not mentioned here, is that severe energy and dynamic constraints exist for four-center, atom exchange reactions. In 1974, King, Dixon, and Herschbach[22] reported results of crossed molecular beam experiments that suggest a new and exciting mechanism

**Table I.** Potential Parameters

| | Atom pair | | | | |
|---|---|---|---|---|---|
| Parameter | $H_2$ | $F_2$ | $Cl_2$ | $Br_2$ | $I_2$ |
| ${}^1D$, eV | 4.7466 | 1.650609 | 2.51002 | 1.991035 | 1.555 |
| $\alpha$, $au^{-1}$ | 1.04435 | 1.5356426 | 1.076959 | 1.039185 | 0.9869 |
| $R_e$, au | 1.402 | 2.67968 | 3.757 | 4.315 | 5.04 |
| ${}^3D$, eV | 1.9668 | 2.0244014 | 0.83369234 | 0.74654029 | 0.7279996 |
| $\beta$, $au^{-1}$ | 1.000122 | 2.0902097 | 0.91 | 0.91 | 0.665 |
| $C$, eV − $au^{-1}$ | 25.55301785 | 5091720.0 | 2559700.0 | 3054600.0 | 3464407.03 |
| $A$, au | 1.0 | −2.8192234 | −3.9107 | −4.2465 | −4.9203 |
| $\sigma$, $au^{-1}$ | 1.6756385 | 4.388149 | 3.152 | 2.938 | 2.569 |
| $R_c$, au | 1.60 | 3.3070845 | 4.40 | 4.80 | 5.50 |

for atom exchange between diatomic molecules that may be an alternative to the slow and constrained four-center mechanism. They employed a nozzle with high pressure and low temperature to produce relatively high concentrations of dimeric chlorine,[23] $(Cl_2)_2$, in a beam crossed with a beam of either $Br_2$ or HI. They had found in earlier experiments[24] of $Cl_2 + Br_2$ and $Cl_2$ + HI that at collision energies as high as 25 kcal/mol that no reactions were detectable; however, in the experiments[22] with dimeric chlorine they detected reaction at collision energies of only ~3 kcal/mol with cross sections that they estimated could be as large as 50 Å$^2$.[25] Durana and McDonald[26] have recently reported studies in which the infrared emission of HF from $F_2 + (HI)_2 \rightarrow$ HF + HI + IF and $F_2 + (HI)_2 \rightarrow$ HF + HI + I + F was detected.

Our purpose here is to explore simple, valence-bond (VB) descriptions of the potential energy surfaces for some six-center bimolecular exchange reactions. Orbital symmetry restrictions (Woodward-Hoffmann rules[27]) predict that four-center, bimolecular exchange reactions are forbidden, but that six-center reactions are not.[22,28] These predictions for the four-center reactions coincide with the results of simple, VB surface formulations such as LEPS (London-Eyring-Polanyi-Sato).[29] Thus it seems reasonable to apply such techniques to six-center reactions.

## Potential Energy Surface Formulation

In 1932, Sherman and Eyring[30] derived the secular equation for the six-electron problem in the spirit of the London equation. The present work begins with this equation. Taylor, Eyring, and Sherman,[31] in 1933, used the formulism to study sodium clusters. Gelb, Jordon, and Silbey[32] recently reported results of a study in which they made a similar application of the theory. Dixon and Herschbach[33] have also used this approach to study six-center reactions, and our results and theirs are in complete accord.[34]

The secular determinant is of the form

$$H_{ij} - ES_{ij} = 0 \tag{1}$$

where the $H_{ij}$ are the integrals

$$H_{ij} = \int \chi_i H \chi_j \mathrm{d}\tau \tag{2}$$

and the $S_{ij}$ are overlap terms

$$S_{ij} = \int \chi_i \chi_j \mathrm{d}\tau \tag{3}$$

We do not give the individual terms of the determinant, but refer the reader to the original paper by Sherman and Eyring.[30] These nonconstant terms consist of Coulombic integrals $Q_{ij}$ and exchange integrals $J_{ij}$, which are functions of the 15 internuclear distances. Rather than solve these integrals we follow the procedures commonly used in LEPS formulations. That is, use is made of the Heitler-London (neglecting overlap) equations:

$${}^1E_{ij} = Q_{ij} + J_{ij} \tag{4}$$

and

$${}^3E_{ij} = Q_{ij} - J_{ij} \tag{5}$$

where ${}^1E_{ij}$ and ${}^3E_{ij}$ are the diatom singlet- and triplet-state energies, respectively. Solving eq 4 and 5 we write the Coulomb and exchange terms as functions of the more easily determined diatomic energies. The singlet-state energy curve for diatom $ij$ is given by the Morse function:

$${}^1E_{ij} = {}^1D_{ij}\,\exp[-2\alpha_{ij}(R_{ij} - R_{eij})] - 2\exp[-\alpha_{ij}(R_{ij} - R_{eij})] \tag{6}$$

where ${}^1D_{ij}$ is the dissociation (including zero-point) energy, $R_{eij}$ is the equilibrium internuclear separation, and $\alpha_{ij}$ is the Morse function exponential parameter. The triplet-state curve for atom pair $ij$ is represented by the Pedersen-Porter[35] functions:

$${}^3E_{ij} = {}^3D_{ij}\,\exp[-2\beta_{ij}(R_{ij} - R_{eij})] + 2\exp[-\beta_{ij}(R_{ij} - R_{eij})] \tag{7}$$

for $R_{ij} \leq R_{eij}$, and

$${}^3E_{ij} = C_{ij}(R_{ij} + A_{ij})\exp[-\sigma_{ij}R_{ij}] \tag{8}$$

for $R_{ij} > R_{eij}$. The parameters ${}^3D_{ij}$, $\beta_{ij}$, $C_{ij}$, $A_{ij}$, and $\sigma_{ij}$ are defined using the method of Raff et al.[5]

The values of the diatomic parameters for $H_2$, $F_2$, $Cl_2$, $Br_2$, and $I_2$, are given in Table I. The parameters for chlorine, bromine, and iodine are those computed by Raff et al.[6] using the method just described.[5] The parameters for hydrogen were computed by Raff et al.[5] by fitting the diatomic curves to the ab initio calculations of Kolos and Roothaan[36] and Kolos and Wolniewicz.[37] The $F_2$ parameters were computed by Blais[38] by adjusting the diatom parameters rather than atomic parameters as in the case of the other halogens. These parameters are those that have been used in a number of trajectory calculations for three- and four-atom systems. On the basis of the agreement with experimental results in these calculations we suggest that they should give reasonable, qualitative results for the systems considered here.

## Results and Discussion

Using the formulism as described above, we have computed the potential energy surfaces for $H_6$, $F_6$, $Cl_6$, $Br_6$, and $I_6$. Because of the approximate nature of these calculations, we make no claims that the results are quantitatively correct; however, based on the past success of transferring potential parameters we do suggest that the results have qualitative significance.

The SCF calculations by Wright[7] show the lowest energy reaction path for $H_6$ passes through a regular hexagonal geometry; this has been confirmed by the CI results of Dixon et al.[8] We have computed the semiempirical $H_6$ energy barrier

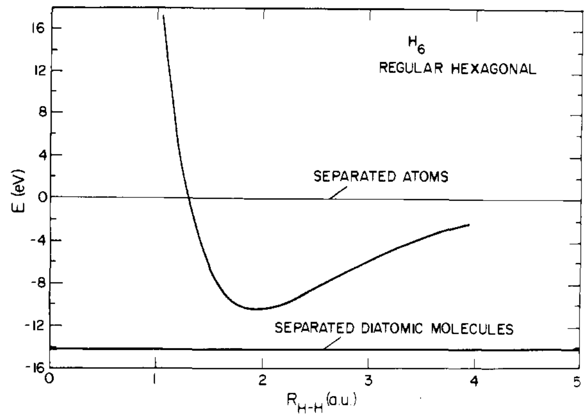

**Figure 1.** Plot of the potential energy of regular hexagonal $H_6$; $R_{H-H}$ is the size of the sides of the hexagon.

for the regular hexagonal configurations. These three calculations are compared in Table II. The semiempirical valence-bond calculation predicts a barrier that is about 20 kcal/mol higher than the best ab initio result.[8] The significant fact is that these calculations predict that $2H_2 + D_2 \rightarrow H_2 + 2HD$ is a possible mechanism of the $H_2$, $D_2$ exchanges, since the $H_6$ energy is less than the energy of $2H_2 + 2H$. Figure 1 shows the behavior of the potential energy of hexagonal $H_6$, relative to separated atoms, as a function the H-H distances of the sides of the hexagon.

The results for the halogens are summarized in Table III. The computed energy barrier for exchange of bonds in $3Cl_2$ is about 8.5 kcal/mol. In molecular beam experiments, Dixon and Herschbach found that the reaction $Br_2 + (Cl_2)_4 \rightarrow 2BrCl + Cl_2$ occurs for collision energies around 3 kcal/mol. Though it may not be completely valid to compare these different chemical systems, it is, we feel, significant that there is qualitative accord for the energy barriers.

It appears that $D_{6h}$ is the lowest energy reaction-path geometry for all these systems. We explored some other geometries, but not to an extent to allow us to say with absolute certainty that $D_{6h}$ is the lowest in energy.

The semiempirical method predicts an increase in energy barrier height with the series Cl, Br, I, F, H. The parameters for the fluorine system were obtained by a different method than used for the other system, and this might account for the relatively high barrier that is computed. The energy barriers for all the systems are high in light of what we know about the energies at which six-center reactions occur;[22,24,26] however, there is qualitative agreement.

It should not be inferred from the present results that the formulation and the values of the parameters that we have used give an "accurate" description of these reactions. However, it is significant that such a simple approach can qualitatively predict that six-center reactions can occur with small energy requirements. Furthermore, it seems reasonable to suggest that this formulation or some modified form of it could provide a method of obtaining a realistic description of the interactions in six-center reactions just as the related formulations (such as LEP and LEPS) have been successful in the case of three- and four-atom reactions.

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**Table II.** Comparison of $H_6$ Reaction Barrier Heights and Locations for SCF,[7] CI,[8] and Semiempirical (this work) Calculations

| Calculation | $E_b$,[a] kcal/mol | $R_b$, au |
|---|---|---|
| SCF[7] | ~90 | 1.86 |
| CI[8] | ≲69 | 1.87 |
| This work | ~88 | 1.95 |

[a] Relative to $3H_2$.

**Table III.** Heights and Locations of Energy Barriers to Exchange for $F_6$, $Cl_6$, $Br_6$, and $I_6$

| System | $E_b$, kcal/mol | $R_b$, au |
|---|---|---|
| $F_6$ | 60.97 | 3.28 |
| $Cl_6$ | 8.50 | 3.97 |
| $Br_6$ | 14.29 | 4.57 |
| $I_6$ | 28.61 | 5.33 |

## References and Notes

(1) (a) Work performed under the auspices of the U.S. Energy Research and Development Agency; (b) Los Alamos Scientific Laboratory; (c) Harvard University; (d) Visiting Staff Member, Los Alamos Scientific Laboratory.
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