Theoret. chim. Acta (Berl.) 19, 390–395 (1970)

# Parameterization in the $H_2I_2$ Potential Surface

FREDRICK L. MINN and ANNE B. HANRATTY*

Department of Chemistry, The George Washington University, Washington, D. C. 20006

Received September 7, 1970

Five types of parameters were found effective in producing a reasonable semi-empirical four-electron valence-bond potential-energy surface for the $H_2I_2$ system. They were (a) the Slater exponents, (b) hybridization of the I orbital, (c) a space scale factor, (d) the I-core penetration energy, and to a more limited extent (e) the ionization potentials. Insignificant or non-physical changes in the surface resulted from alterations in (a) the integral approximations, (b) values of the electron affinities, and (c) orientation dependence of the *p* orbitals.

Attempts to understand more precisely the rates and mechanisms of reactions of very small molecules have produced an enormous interest recently in extensive collision-theory calculations. Generous amounts of information can be obtained from relatively minimal effort. At the heart of such computations lies the problem of obtaining a good potential-energy surface. *A priori* surfaces have been generated for the simplest systems [1] (e. g., $H_3$, $H_4$, and $NH_4Cl$); semiempirical surfaces have likewise been produced with success [2] (e. g., $H_3$, $H_4$, and $H_2I_2$). This last, the $H_2I_2$ system, proved especially interesting when Sullivan's photochemical experiments showed that the presumed one-step mechanism for formation of HI from the elements at ordinary temperatures was incorrect [3]. We have reported the barrier heights obtained from a four-electron valence-bond calculation of the $H_2I_2$ potential surface [4]; here we offer some of our findings concerning the effects of various parameterizations on the shape of the $H_2I_2$ surface and energy of the activated complex.

## Model

The four-body system was chosen to consist of two protons, two polarizable $I^+$ cores, and four electrons. Slater determinants corresponding to the two independent covalent bonding arrangements were constructed from four Slater-type orbitals, one centered on each nucleus [5]. The usual $2 \times 2$ secular equation was then constructed and solved, using Pariser's [6], Pople's [7], and Mulliken's [8] approximations for all integrals except the overlaps, which were evaluated analytically; no integral was set to zero arbitrarily. All parameters were adjusted to give the experimental diatomic energies, the experimental reaction exothermicity, and reasonable diatomic bond distances; any remaining flexibility in the parameterization was used to minimize the barrier height [4] for the $C_{2v}$ trapezoidal conformation.

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* NASA Predoctoral Fellow, 1966–1969, NSF Predoctoral Fellow, 1969–1970. Taken in part from the Ph. D. thesis of ABH, 1970. Present address of ABH: Department of Chemistry, Whittier College, Whittier, California 90608.

## Results and Discussion

The least heavily parameterized case incorporated the integral approximations and the two Slater exponents $\zeta_I$ and $\zeta_H$ for the $p$ and $s$ orbitals on iodine and hydrogen, respectively. Within these constraints the results were unsatisfactory: The diatomic-limit energies could be optimized only to within 5, 6, and 30% of the experimental values for $H_2$, HI, and $I_2$, respectively, and the lowest lying reaction path, the $D_{\infty h}$ geometry, was 1.7 eV above the experimental activation energy. The calculated diatomic equilibrium distances were almost universally too small, in agreement with a similar phenomenon found by Pohl and Raff in their theoretical study on interhalogens [9], and the reaction exothermicity could be optimized only to about double the experimental value. From this extremely simplified model one obtains a contour map whose features are qualitatively correct but whose details lead to rates far slower than experimental. Consequently, elaborations on the model were undertaken and are partially summarized in Tables 1 and 2. Unfortunately, no parameter was independent of any other and a full reoptimization was needed for each alteration in the model.

Because of the proximity of the 5$s$ and 5$p$ energies in the iodine atom, some 5$s$ character was added to the iodine valence orbitals $\phi_I$; the 5$s$ orbital exponent was not varied but was taken to be identical to that of the 5$p$. Thus we chose $\phi_I = 1/(1+a^2)^{\frac{1}{2}}\,\phi_{5p} + a/(1+a^2)^{\frac{1}{2}}\,\phi_{5s}$, where $a$, the mixing coefficient, became as great as 0.24. This value corresponds to about 6 % 5$s$-character and is only somewhat less than values found by Pohl and Raff [9]. The effects of increasing $a$ were pronounced, serving principally to increase both the $I_2$ bond energy and the barrier height. Although the addition of a 5$d$ orbital or another $p$ orbital was not examined, it seems likely that these too would exert comparable influence on the surface, since the $p$ orbitals are insensitive to changes in orientation. Hence, the $s$ orbital, or any other added orbital, tends to correct the relative amplitudes of the iodine valence wave function in the near and far regions from the nucleus. This assertion is based on an attempt to lower the energy of the activated complex by altering the manner in which the iodine $p$ orbitals orient themselves when approached by the other atoms. Unlike the diatomic molecules examined by Pohl and Raff [9], this 4-atom system includes some $\pi$ bonding, principally in the region of the saddle point. In most of our calculations an (unnormalized) orientation function $f(r_{Ij})$ was used which weighted the direction from iodine I to atom $j$ according to the equation $f(r_{Ij}) = \exp[(1 - r_{Ij}/r_{Ij,\mathrm{eq}})^2]$; this served to emphasize $\sigma$ bonding with the nearer atoms and to reduce $\sigma$ bonding with the farther. An alteration of this orientation function to a less severe $f(r_{Ij}) = r_{Ij}/r_{Ij,\mathrm{eq}}$ produced changes of only a few tenths of a percent in the surface. Perhaps this is not too surprising, since the iodine orbitals are very diffuse and since the $\sigma$ and $\pi$ components of overlap usually differ by less than a factor of four.

Because the iodine cores are ill represented by point charges, corrections were made for penetration of the core by another atom and for polarization of the charge cloud. For a proton $j$ in the vicinity of iodine, the effective charge $Q_I$ seen by the proton was taken to be $Q_I = 1 + 51.29056 \exp(-2.4093\, r_{Ij})$; this equation gave a close fit to the tabulated Hartree-Fock potentials given by Herman

Table. 1. *Parameter values in the most and least heavily parameterized cases. In atomic units*

| Parameter | Least | Most | Experiment |
|---|---|---|---|
| $\zeta_H$ | 1.15 | 0.96 | 1.0[a] |
| $\zeta_I$ | 1.425 | 2.35 | 1.9[a] |
| *IP*(H) | 0.5 | 0.55 | 0.5[b] |
| *IP*(I) | 0.422 | 0.4636 | 0.422[b] |
| *EA*(H) | −0.02745 | −0.02745 | −0.02745[b] |
| *EA*(I) | −0.1191 | −0.1191 | −0.1191[b] |
| *a* | 0 | 0.24 | — |
| $\lambda$ | 1.00 | 1.05 | — |
| $Q_I$ | 1.00 | varies with distance | — |
| $r^*$ | 0 | 1.8 | — |
| $Z_{eff}$ | 1.425 | 1.00 | — |

[a] By Slater rule's. Slater, J. C.: Physic. Rev. **36**, 57 (1930).

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Table 2. *Estimated effects of changes in the parameters. Entry* (+0.5, −0.1) *is to be read "if row head is increased by* 0.5, *the cloumn head is decreased by* 0.1." *Energies in* eV; *other values in atomic units. The values are mean to be suggestive rather than quantitative*

| | Barrier Height | Exothermicity | $I_2$ Energy | $H_2$ Energy | HI Energy | $I_2$ Distance | $H_2$ Distance | HI Distance |
|---|---|---|---|---|---|---|---|---|
| $\zeta_H$ | | | none | (+0.02, +0.16) | | none | (+0.02, −0.03) | |
| $\zeta_I$ | (+0.0475, −0.2) | | (+0.1, +0.1) | none | (+0.1, −0.06) | (+0.1, −0.1) | none | |
| *IP*(H) | | (−0.05, +0.05) | none | (−0.05, +0.28) | (−0.05, +0.12) | none | | |
| *IP*(I) | | (−0.08, +0.17) | (−0.08, −0.28) | none | (−0.08, +0.18) | none | | |
| *EA*(H) | | (−0.01, +0.07) | none | none | none | none | none | none |
| *EA*(I) | | (−0.01, +0.07) | none | none | none | none | none | none |
| *a* | (+0.05, +0.3) | (+0.01, +0.05) | (+0.05, +0.2) | none | | | none | |
| $\lambda$ | | (+0.05, +0.12) | (+0.05, +0.75) | (+0.05, +1.75) | (+0.05, +1.15) | none | (+0.05, +0.7) | (+0.05, +0.05) |
| $r^*$ | (+, −) | (+0.2, +0.4) | (+0.2, −0.3) | none | none | (+0.2, +0.1) | none | none |
| $Z_{eff}$ | | (+0.3, +0.3) | (+0.3, +1.16) | none | (+0.3, +0.72) | (+0.3, −0.1) | none | variable |

and Skillman in their work on atoms [10]. For two iodine atoms near one another the same equation was used. However, $r_{Ij}$ was not the actual distance between the two nuclei but rather was the actual separation reduced by an adjustable constant $r^*$, which reached 1.8 a.u. in the best case studied. The effect of introducing $r^*$ was to accommodate the alteration in geometry of the two very bulky iodine cores by allowing their nuclei to approach closer than one would predict from their "edge-to-edge" distances; it is roughly equivalent to moving the overlapping portions of the charge clouds to the farther regions. Introduction of the Herman-Skillman data with $r^* = 0$ allowed calibration of the diatomic limits to experiment without affecting significantly the barrier height. Increase of $r^*$ produced the expected increase in the $I_2$ repulsion energy with its attendant decrease in $I_2$ bond strength and increase in $I_2$ bond distance. The decrease in the $I_2$ bond strength produced a rise in the $H_2 + I_2$ conformation energy relative to both HI and $H_2I_2$ and yielded, as a consequence, both a significantly lower barrier energy and a lower exothermicity.

One integral, the one-center nuclear attraction energy, contains a factor $Z_{\mathrm{eff}}$, the effective charge seen by the electron attracted to its own nucleus. For hydrogen atoms, the parameter $Z_{\mathrm{eff}}$ is straightforwardly unity. Since, however, for iodine, an electron-core penetration, similar to the core-core penetration, makes a unipositive I-core unrealistic, $Z_{\mathrm{eff}}$ was taken initially to be the same [11] as the effective nuclear charge (Slater exponent) $\zeta_{\mathrm{I}}$ of the iodine orbital; $Z_{\mathrm{eff}}$ was then allowed to vary, independent of $\zeta_{\mathrm{I}}$. Values of $Z_{\mathrm{eff}}$ ranged from 1.00 to 2.35, and attempts to make $Z_{\mathrm{eff}}$ larger, to approach the value 4.69 found by Raff, Stivers, Porter, Thompson, and Sims [2j] for a similar parameter, resulted in major distortions of the surface with $I_2$ bond energies far too large. Most amazing, perhaps, is the fact that $Z_{\mathrm{eff}}$ optimized to 1.00 with concomitant pronounced lowering of the trapezoidal barriers in the most heavily parameterized case. No physical reason for this reduction to the point-charge model is apparent to us and we must lay this value at the door of compensation-of-errors inherent in the overall approximation.

Fundamental to this calculation were the integral approximations. It is generally conceded [12] that the Mulliken approximation [8], $\phi_i\phi_j = (\phi_i^2 + \phi_j^2)\, S_{ij}/2$, becomes worse as the two nuclei $i$ and $j$ get farther apart. Following an error analysis by Cizek [12], we attempted a correction of the form $\phi_i\phi_j = (\phi_i^2 + \phi_j^2)\, S_{ij}/2g(r_{ij})$, where $g(r_{ij}) = 1$ for $r_{ij} < 1.3$ a.u., $g = 1 + 0.0862\,(r_{ij} - 1.3)$ for 1.3 a.u. $\leqq r_{ij} < 4.2$ a.u., and $g = 1.25$ for $r_{ij} \leqq 4.2$ a.u. This and further attempts to correct the integrals themselves from Cizek's data resulted in $I_2$ bond energies near zero and were abandoned. Likewise, the Wolfsberg-Helmholz [13] parameter $k$, $\phi_i\phi_j = k(\phi_i^2 + \phi_j^2)\, S_{ij}/2$, used with success by others [9], led unproductively to very small $H_2$ and very large $I_2$ internuclear distances. A suggestion of Reudenberg [14] that in two-center one-electron integrals the orbital product $\phi_i\phi_j$ can be replaced by $(\phi_i^2 + \phi_j^2)\, S_{ij}^2/2$ led to results essentially like those obtained by introduction of the Wolfsberg-Helmholz parameter. Thus the Mulliken approximation works remarkably well in a system in which it is expected to have some shortcomings. That is, the diatomic-limiting conformations, which are calculated with as many as five of the six independent internuclear distances very large, are ultimately compared, on a reaction-coordinate diagram, with the saddle point conformation, its atoms all relatively close. Any distance dependence of the errors could explain at least partly why no surface examined had a barrier height as low as the measured activation energy and why no set of parametric values allowed us to reproduce the simpler Heitler-London-type surface of Raff, Stivers, Porter, Thompson and Sims [2$j$]. It appears likely that the approximations were depressing the diatomic energies while leaving the activated complex essentially uncorrected. A similar high-barrier artifact is almost certainly present in any calculation which is entirely covalent; specifically here, ionic terms would undoubtedly be more important when the atoms are nearby (saddle point) than when they are far apart (diatomic limits).

Pariser's approximation, $\langle \phi_i \phi_i | r_{12}^{-1} | \phi_i \phi_i \rangle = IP(i) + EA(i)$, was modified, as well, by allowing the ionization potentials ($IP$) and electron affinities ($EA$) to vary by small amounts from their experimental values. In agreement with others [15], $IP$(I) was taken to be that of the valence state; the argument for such an assumption has been given by Hinze and Jaffe [16]. Furthermore, because our iodine valence orbitals contained approximately 6% 5*s* character, the use of 0.464 eV instead of the free-atom 0.422 eV was considered appropriate. The $IP$(H) was also taken to be about 10% higher than experimental – on a somewhat more cavalier application of the same argument. Alteration of the ionization potentials within a range still physically meaningful produced significant changes, generally decreasing the barrier height and increasing other energies by decreasing the $IP$'s. On the other hand, changes in the $EA$'s only slightly outside the range of experimental values reported had virtually no effect on the surface. The $IP$ enters the formula for the total energy twice, in Pariser's approximation to the one-center repulsions and in the approximate-eigenvalue integrals $| -1/2\ \nabla^2 - Z_{\text{eff}}\, e^2/r_i | \phi_i \rangle = -IP(i) | \phi_i \rangle$; $EA$ enters only once. Therefore, it may be that the primary source of the effect is the approximate-eigenvalue integrals. Those parts of the hamiltonian that were close to being eigenoperators of the orbital wavefunctions were sorted away from the rest, in an attempt to separate the two effects. The behavior of such a sorting was much the same as varying $Z_{\text{eff}}$, for the wavefunction misses being an eigenfunction primarily by the magnitude of its Slater exponent.

Finally, a recomputation was made upon introduction of a space scale factor $\lambda$, in order to partition the energies correctly [17, 18]. Since the kinetic $\langle T \rangle$ and potential $\langle V \rangle$ energies were calculated separately, they could be compared for any conformation, in particular that at the saddle-point. With $\lambda \sim -\langle V \rangle / 2 \langle T \rangle$ from the activated complex, reevaluation of the entire surface was made. The barrier height decreased markedly and both the bond lengths and bond energies increased upon setting $\lambda$ to 1.05; this value was not quite large enough to make the system obey the virial theorem, but its effect was clearly defined.

## Summary

The most profound effects upon the 4-electron covalent valence-bond $H_2I_2$ surface were produced by changes in (a) the orbital exponential parameters, (b) hybridization of the iodine valence orbital, (c) the energy partition through the space scale factor, (d) the degree of iodine-core penetration, and (e) the ionization potentials. Alterations in the integral approximations, electron affinities, and orientation dependence of the *p* orbitals led to no significant differences in the surface. The inability to obtain a barrier whose height is the activation energy is probably due to omission of ionic contributions. Because in all cases studied the linear conformation of nuclei had a lower barrier than did the trapezoidal, we suggest that prediction of the atomic mechanism might have predated its discovery, since a linear activated complex is not physically accessible to the elementary molecules.

*Acknowledgement.* We thank the University Computer Center for generosity in computer time on the IBM 360/50.

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Professor
Fredrick L. Minn
Department of Chemistry
The George Washington University
Washington, D. C. 20006, USA