Potential energy surface for the hydrogen–iodine reaction

James B. Anderson

Articles you may be interested in

Potential energy surface for the hydrogen–iodine reaction

James B. Anderson

Department of Chemistry, Pennsylvania State University, University Park, Pennsylvania 16802

The potential energy surface for the H_2–I_2 system was determined in analytic variational electronic structure calculations with single- and double-substitution configuration interactions for the 16 valence electrons and with effective potentials for the iodine core electrons. The favored pathway for the overall reaction $H_2+I_2 \rightarrow HI+HI$ was found to pass through the region of the collinear configuration I–H–H–I. The pathway is accessible to bound and unbound iodine atom pairs and it allows the bimolecular and termolecular reactions, $H_2+I_2 \rightarrow HI+HI$ and $H_2+I +I \rightarrow HI+HI$, both proposed by Bodenstein 100 years ago.

One hundred years ago Max Bodenstein published his landmark paper[1] describing his measurements of the chemical kinetics of the hydrogen–iodine reaction, $H_2+I_2 \rightarrow HI +HI$. He reported rate measurements of the forward and reverse reactions and observed that below about 700 K these reactions follow overall second order kinetics as expected for elementary bimolecular reactions. The reactions became "textbook" examples of bimolecular reactions. Bodenstein discussed other possible reaction mechanisms and noted that the termolecular reaction involving "the combination of existing iodine atoms with hydrogen would have to be looked (at): $2I+H_2 \rightarrow 2HI$... ."[2] It is now believed that below abut 600 K[3–5] reaction occurs by both bimolecular and termolecular mechanisms, as summarized in Table I, and that above about 750 K a chain mechanism, at least partly anticipated by Bodenstein,[2] becomes dominant.[5–7]

We report here the results of modern electronic structure calculations which predict the energetically favored reaction pathway passes through a collinear configuration I–H–H–I with the iodine atoms separated by about 6 Å. Reaction on the calculated potential energy surface occurs by insertion of H_2 between two I atoms which may be those of a bound or quasibound I_2 molecule stretched nearly to dissociation (bimolecular mechanism)[4] or may be two unbound I atoms passing near each other (termolecular mechanism).

The earliest calculations of the potential energy surface for the H_2–I_2 system were semiempirical London–Eyring–Polanyi (LEP) calculations by Wheeler, Topley, and Eyring[8] which predicted reaction to occur through a trapezoidal transition state. Much later, Hoffmann[9] presented arguments based on orbital symmetry suggesting the trapezoidal geometry to be energetically unlikely, and Cusachs, Kreiger, and McCurdy[10] reported 16-electron semiempirical molecular-orbital calculations suggesting the activation barrier to be lower for a collinear geometry than for a trapezoidal geometry. Raff *et al.*[11] used a semiempirical four-electron valence bond formalism to obtain a complete potential energy expression of the London–Eyring–Polanyi–Sato (LEPS) type. Their surface allows reaction through both[3] the trapezoidal configuration (barrier 42.0

kcal/mole above the minimum for separated H_2 and I_2) and the collinear configuration (barrier 45.6 kcal/mole). In similar four-electron valence bond calculations Minn and Hanratty[12] found the trapezoidal barrier slightly higher than the collinear, but both barriers were about 50% higher than the experimental activation energy of 40.6 kcal/mole.[2,13–15]

Our calculations for the system were analytic variational calculations with single and double substitution configuration interactions for the 16 valence-shell electrons. An effective core potential was used to replace the 46 electrons corresponding to the $Kr(4d)^{10}$ inner-shell electrons of each iodine atom. A $3s3p$ Gaussian basis contracted to $2s2p$ was used to treat the $5s$ and $5p$ valence orbitals of iodine. The basis set and pseudopotentials were those developed by Hay and Wadt[16] which have been incorporated into GAUSSIAN 92 programs under the name LANL1DZ. The calculations were run as standard GAUSSIAN programs.[17]

We tested the accuracy of the calculations by comparing results for known properties of the H_2–I_2 system. Potential energy curves calculated for the diatomics H_2, HI, and I_2 were found to be at least qualitatively correct in comparisons with the known curves (known values in parentheses): H_2, $D_e=98.0(109.5)$ kcal/mole, $R_e=0.75(0.74)$ Å; HI, $D_e=64.4(73.7)$ kcal/mole, $R_e=1.65(1.60)$ Å; I_2, $D_e=25.7(35.8)$ kcal/mole, $R_e=2.92(2.67)$ Å. The calculated collinear barrier height for the reaction $H+I_2 \rightarrow HI+I$ was 0.4 kcal/mole, a value close to the measured activation energy of 0.0 kcal/mole,[14] and the calculated collinear barrier height for the reaction $H+HI \rightarrow H_2+I$ was 2.7 kcal/mole, a value reasonably close to the measured activation energy of 0.5 kcal/mole.[7] Each of these properties is qualitatively correct and this suggests we may expect predictions for the H_2–I_2 reaction to be qualitatively correct.

In exploratory calculations of a variety of pathways for the hydrogen–iodine reaction we found the potential energy surface to be similar in form to the semiempirical LEPS surface obtained by Raff *et al.*[11] and to our own *ad hoc* modification of that surface with higher energies in the trapezoidal region.[4] As we observed in earlier work[3,4]

TABLE I. Bimolecular and termolecular mechanisms for the overall reaction $H_2 + I_2 \rightarrow HI + HI$. Mechanisms 3 and 4 are more specific statements of mechanisms 1 and 2.

Bimolecular		
	$H_2 + I_2 \rightarrow HI + HI$	(1)
Termolecular		
	$I_2 + M \rightleftharpoons I + I + M$	
	$H_2 + I + I \rightarrow HI + HI$	(2)
Bimolecular		
	$I_2 + M \rightleftharpoons I_2(hi\ v) + M$	
	$H_2 + I_2(hi\ v) \rightarrow HI + HI$	(3)
Termolecular		
	$I_2 + M \rightleftharpoons I_2(hi\ v) + M$	
	$I_2(hi\ v) + M \rightleftharpoons I + I + M$	
	$H_2 + I + I \rightarrow HI + HI$	(4)

FIG. 2. Calculated potential energy surface in $(R_{H,H}, R_{I,I}, R_{H_2,I_2})$ space. The curves are potential energy contours 5.0 kcal/mole above the energy of the saddle point. Angles are as shown in Fig. 1. The configuration $(H_2 + I + I)$ lies in the broad rising channel, $(H_2 + I_2)$ lies in the cul-de-sac channel at the lower right, and $(HI + HI)$ lies in the channel exiting toward the viewer.

with these surfaces the lowest-energy reaction pathways occur for symmetric configurations with all four atoms in a plane as shown in Fig. 1. Variations from the symmetry shown were found to increase the potential energies for configurations along reaction pathways. The low-energy configurations of interest in considering reactions are thus limited to those with the geometry of Fig. 1 with only three remaining variables, the distances $R_{H,H}$, $R_{I,I}$, and R_{H_2,I_2}. Low-energy reaction pathways may then be traced in the three-dimensional space illustrated in Fig. 2.

In calculations for a large number of configurations the lowest-energy reaction path was found to pass through a symmetric collinear configuration with a saddle point at $R_{H,H} = 0.75$ Å, $R_{I,I} = 5.95$ Å, having an energy 35.1 kcal/mole above the minimum for separated H_2 and I_2. This minimum in the barrier occurs for $R_{H_2,I_2} = 0$, i.e., in the first plane from the left in Fig. 2. The minimum in the barrier rises slowly with increasing R_{H_2,I_2} from 35.1 kcal/mole for $R_{H_2,I_2} = 0$ to 36.0 kcal/mole for $R_{H_2,I_2} = 1.0$ Å and increases more rapidly thereafter to 57.5 kcal/mole at $R_{H_2,I_2} = 1.75$ Å. No saddle point corresponding to a trapezoidal configuration is observed. As shown in Fig. 3 the minimum in the barrier rises monotonically as the configuration of the saddle point is deformed to a trapezoidal configuration.
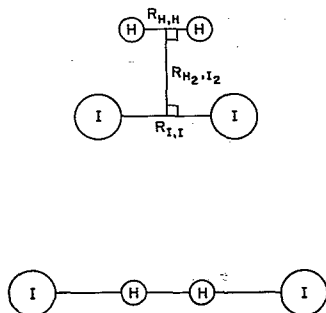
The reaction channel is not severely restricted to the collinear pathway. The 0.9 kcal/mole increase in the barrier height E_b for distortion from collinear to $R_{H_2,I_2} = 1.0$ Å reduces the exponential factor $\exp(-E_b/kT)$ for 600 K to about one half of its value at the collinear saddle point. Since the configuration space available for passage through the region varies as R_{H_2,I_2}^2, trajectories may be expected to cross the barrier with R_{H_2,I_2} distributed in the range of 0 to 1.5 Å.

The calculated surface is most similar to the *ad hoc* LEPS surface, modified to favor the collinear pathway, for which we observed both bimolecular and termolecular reactions in classical trajectory calculations.[4] As noted previously, slight variations in the potential energy surface might favor either bimolecular or termolecular reaction.

FIG. 1. Symmetric trapezoidal and collinear configurations lying on prospective pathways for the hydrogen–iodine reaction. Distortion of any of the angles increases the potential energy for most configurations similar to those shown.
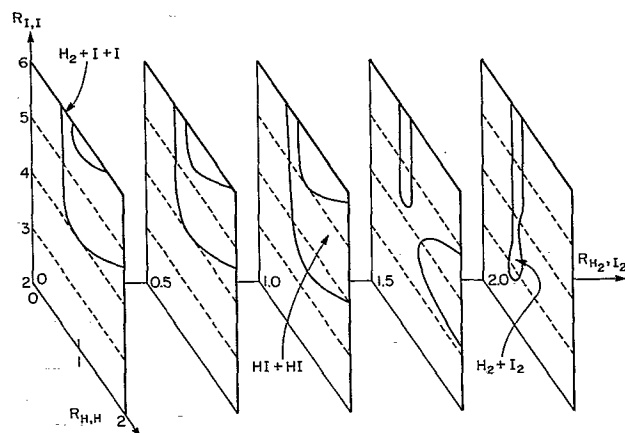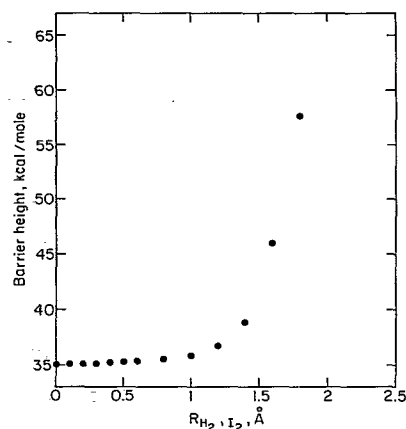
FIG. 3. Minimum in the barrier to reaction with constraint to fixed values of R_{H_2,I_2}. The overall minimum occurs for the collinear configuration $(R_{H_2,I_2} = 0)$.

The question of bimolecular vs termolecular reaction was not resolved by Sullivan's[18] experimental measurements of the kinetics of the overall reaction $H_2 + I + I \rightarrow HI + HI$. We have argued[4] that if relaxation of vibrationally excited $I_2(hi\ v)$ formed in recombination is slow, $I_2(hi\ v)$ may exist nearly in equilibrium with I atoms and the bimolecular and termolecular reactions may be kinetically indistinguishable in Sullivan's experiments. Recent measurements by Nowlin and Heaven[19] have shown vibrational relaxation of $I_2(v=43)$ to be slow for collisions with He and O_2 and immeasurably slow for collisions with Ar and I_2. The elimination of the trapezoidal pathway for reaction is consistent with these observations. Trajectories following the trapezoidal pathway on the surface of Raff et al.[11] were found to originate from reactant I_2 molecules at low levels of vibrational excitation inconsistent with Sullivan's measurements.

The potential energy surface calculated by modern quantum mechanical methods appears adequate to explain, at least qualitatively, all available experimental observations for the hydrogen–iodine reaction. These include reaction rate, kinetics first order in H_2 and in I_2 for thermal systems, vibrational excitation of the HI products, as well as rate, kinetics, and excitation of reactants[20,21] for the reverse reaction. Determination of the correct mechanism for reaction—bimolecular or termolecular or both—requires a potential energy surface more accurate than the one we have calculated. We hope that the required accuracy as well as a definitive experiment will soon be available. At present, although both bimolecular and termolecular reactions[4] are most likely, the question of bimolecular vs termolecular is not completely resolved 100 years after Max Bodenstein raised it.

[1] M. Bodenstein, Z. Physik. Chem. **13**, 56 (1894).
[2] See Ref. 1, p. 122.
[3] R. L. Jaffe, J. M. Henry, and J. B. Anderson, J. Am. Chem. Soc. **98**, 1140 (1976); J. M. Henry, J. B. Anderson, and R. L. Jaffe, Chem. Phys. Lett. **20**, 138 (1973); J. B. Anderson, J. M. Henry, and R. L. Jaffe, J. Chem. Phys. **60**, 3725 (1974).
[4] J. B. Anderson, J. Chem. Phys. **61**, 3390 (1974).
[5] K. J. Laidler, *Chemical Kinetics* (Harper and Row, New York, 1987), 3rd ed., pp. 298–300.
[6] S. W. Benson and R. Srinivasan, J. Chem. Phys. **23**, 200 (1955).
[7] J. H. Sullivan, J. Chem. Phys. **30**, 1292 (1959).
[8] A. Wheeler, B. Topley, and H. Eyring, J. Chem. Phys. **4**, 178 (1936).
[9] R. Hoffmann, J. Chem. Phys. **49**, 3739 (1968).
[10] L. C. Cusachs, M. Kreiger, and C. W. McCurdy, J. Chem. Phys. **49**, 3740 (1968).
[11] L. M. Raff, L. Stivers, R. N. Porter, D. L. Thompson, and L. B. Sims, J. Chem. Phys. **52**, 3449 (1970).
[12] F. L. Minn and A. B. Hanratty, J. Chem. Phys. **53**, 2543 (1970); Theor. Chim. Acta **19**, 390 (1970).
[13] J. H. Sullivan, J. Chem. Phys. **30**, 1577 (1959).
[14] J. H. Sullivan, J. Chem. Phys. **36**, 1925 (1962).
[15] J. H. Sullivan, J. Chem. Phys. **39**, 300 (1963).
[16] P. J. Hay and W. R. Wadt, J. Chem. Phys. **82**, 299 (1985).
[17] M. J. Frisch, M. Head-Gordon, H. B. Schlegel, K. Raghavachari, J. S. Binkley, C. Gonzalez, D. J. Defrees, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. L. Martin, L. R. Kahn, J. J. P. Stewart, E. M. Fluder, S. Topiol, and J. A. People, GAUSSIAN 92 (Gaussian Inc., Pittsburgh, PA, 1993).
[18] J. H. Sullivan, J. Chem. Phys. **46**, 73 (1967).
[19] M. L. Nowlin and M. C. Heaven, J. Chem. Phys. **99**, 5654 (1993).
[20] S. B. Jaffe and J. B. Anderson, J. Chem. Phys. **51**, 1057 (1969).
[21] H. Horiguchi and S. Tsuchiya, Int. J. Chem. Kinetics **13**, 1085 (1981).