

Mechanism of the bimolecular(?) hydrogen-iodine reaction

James B. Anderson

Yale University, New Haven, Connecticut 06520

(Received 20 February 1974)

A combined phase-space/trajectory study of the hydrogen-iodine exchange reactions (overall, $H_2 + I_2 \rightarrow HI + HI$) was carried out for a LEPS potential energy surface modified to favor reaction through the collinear reaction configuration. The results show reaction to occur by both bimolecular and termolecular mechanisms involving pairs of iodine atoms with energies slightly below (bimolecular) or slightly above (termolecular) the dissociation limit. Together with other considerations this finding suggests that in stating the reaction proceeds by the bimolecular mechanism the old textbooks *may* have been correct. A detailed comparison with Sullivan's photochemical experiments requires a knowledge of the iodine-atom recombination process which is not presently available. Sullivan's primary conclusion, i.e., the iodine species participating in the exchange reaction are the same as those in the slow step of recombination, is upheld; but, the experimental distinction between bimolecular and termolecular mechanisms depends on the question of the relative rates of recombination and relaxation of iodine.

INTRODUCTION

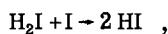
Until Sullivan's investigation¹ of the photochemical production of hydrogen iodide in hydrogen-iodine systems, the reaction of hydrogen with iodine was considered to occur by the elementary bimolecular reaction,



Sullivan found the rate of reaction to be proportional to the square of the concentration of photochemically produced iodine atoms and interpreted his data as consistent with the elementary termolecular reaction,



with a mechanism involving the intermediate H_2I ,



and with a mechanism involving I_2^* , an atomic pair² with more internal energy than the dissociation energy of I_2 ,



Reaction (4) is a more explicit description of Reaction (2).

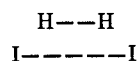
Sullivan's experiments clearly showed the photochemical formation of HI involves species which react in the rate-determining step of iodine-atom recombination. On the basis that the rate-determining step is not vibrational relaxation, Sullivan concluded the rate-determining step in HI formation can not be reaction of H_2 with vibrationally excited I_2 ,



Reaction (5) is a more explicit statement of the bimolecular reaction (1). The species $I_2(\text{hi } \nu)$ is defined as vibrationally excited I_2 with internal energy near but less than the dissociation energy I_2 .

Following Sullivan's work it has been argued that the termolecular reaction (2) occurs by passage through a collinear transition configuration $I \cdots H \cdots H \cdots I$ inaccessible to the molecular reactants of (1).^{3,4} Considera-

tion of molecular orbital symmetry arguments has suggested the trapezoidal transition configuration



has a potential energy too high to allow reaction to occur at significant rates.³⁻⁵ However, as noted by Porter and Raff,^{6,7} such arguments *alone* are not sufficient to determine the relative barrier heights for the H_2, I_2 system.

However, it should be recognized that an I_2 molecule excited to a vibrational energy near the dissociation energy stretches to an internuclear distance of 5.0 Å or more at the outer turning point of vibration. Moving at a relatively high velocity in comparison to the I atoms, an H_2 molecule may approach from the side and insert between the I atoms to produce the collinear configuration $I \cdots H \cdots H \cdots I$. This configuration is directly accessible to the molecular reactants H_2 and I_2 . Reactions of H_2 with unbound² I-atom pairs (I+I) and quasi-bound² pairs $I_2(\text{qb})$ may occur in a similar manner.

There have been two sets of trajectory calculations for the (H_2, I_2) system, each using the potential energy of the LEPS type devised by Raff *et al.*⁸ This surface favors reaction through the trapezoidal configuration across a barrier of 42.0 kcal/mole relative to the minimum for separated H_2 and I_2 . The barrier in the collinear configuration is slightly higher at 45.6 kcal/mole. The first set of calculations, by Raff *et al.*,⁹ was incomplete and omitted several reactant combinations. The second set, a combined phase-space trajectory study by Jaffe *et al.*,¹⁰⁻¹² showed reaction to occur primarily through the trapezoidal configuration with H_2 and I_2 as reactants and to a lesser extent through the collinear configuration with H_2 and I_2 , H_2 and $I_2(\text{qb})$, and H_2 and (I+I) as reactants. For reaction through the trapezoidal configuration the reactant I_2 was found to be vibrationally excited, in the range 5-25 kcal/mole. This excitation is probably too low for agreement with Sullivan's experiments.

For the present study we revised the LEPS surface of the earlier studies by lowering the barrier in the region

TABLE I. Dividing surface sections.^a

Section (k)	Range					i_k (10^{-78}cm^6)	k_{e_k} ($\text{cm}^3\text{mole}^{-1}\cdot\text{sec}^{-1}$)
	a_k	b_k	$c_k(\text{\AA})$	$R_{\text{HH}}(\text{\AA})$	$R_{\text{H}_2, \text{I}_2}(\text{\AA})$		
A	2.0	-2.0	8.8	0.6-1.2	0-0.8	136	15.6
B	1.0	-1.0	4.8	0.6-1.2	0.8-1.6	204	12.8
D	0	0	1.6	0.6-1.1	1.6	66	1.86
E	1.0	0	0.5	1.1-2.1	1.6-2.1	7	0.44

^aRate constant k_{e_k} for equilibrium at 700 °K specified in terms of reactants $\text{H}_2 + \text{I}_2$.

of the collinear configuration and raising it in the region of the trapezoidal configuration. We have repeated our combined phase-space/trajectory study following procedures identical to those described previously.¹⁰

POTENTIAL ENERGY SURFACE

The LEPS surface of Raff *et al.*⁸ was revised by adjusting the triplet energies for I_2 and HI to 1.30 and 0.82, respectively, of their previous values and by adding to the potential energy a term V^* given by

$$V^* = D^* \exp\{-a[(R_{\text{HH}} - R'_{\text{HH}})^2 + (R_{\text{II}} - R'_{\text{II}})^2 + (R_{\text{H}_2, \text{I}_2} - R'_{\text{H}_2, \text{I}_2})^2]\}, \quad (6)$$

with the constants $D^* = 10$ kcal/mole, $a = 0.16 \text{\AA}^{-2}$, $R'_{\text{HH}} = 0.7 \text{\AA}$, $R'_{\text{II}} = 3.0 \text{\AA}$, and $R'_{\text{H}_2, \text{I}_2} = 1.6 \text{\AA}$. The resulting barrier heights for the collinear and trapezoidal regions are 39.6 and 43.5 kcal/mole, respectively, above the minimum for separated H_2 and I_2 .

The modifications have little effect on the relatively low barriers for the reactions $\text{H} + \text{I}_2 \rightarrow \text{HI} + \text{I}$ and $\text{H}_2 + \text{I} \rightarrow \text{HI} + \text{H}$. The original surface, while giving an acceptable rate constant in trajectory calculations^{13,14} for the reaction $\text{H} + \text{I}_2 \rightarrow \text{HI} + \text{I}$, fails to produce the sideways scattering of HI observed by McDonald *et al.*¹⁵ in crossed-beam experiments. Another characteristic of the original surface, a well for the configuration HHI is probably too deep as shown in measurements of elastic scattering of H_2 from I by Lee *et al.*¹⁶ The revisions to the surface offer no corrections for these defects.

EQUILIBRIUM RATES

The locations of sections of the dividing surface were similar to those in the earlier study with sections A and D in the regions of the collinear and trapezoidal configurations, respectively. Section C of the earlier study was eliminated by extending surface D. The constants a_k , b_k , and c_k are listed in Table I together with the integrals i_k and equilibrium flux constants at 700 °K for each section.

RESULTS

A total of 430 trajectories crossing the dividing surface for 700 °K were examined in trajectory calculations as in Ref. 10. Of these 163 were successful, originating from reactants and passing directly to products without recrossing the dividing surface. The details for each section of the surface are given in Table II, which lists

the conversion coefficients ξ_k (number successful/number of trials) and the reactant distributions.

The calculated rate constant for the over-all reaction, written as $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$, at 700 °K is $11.6 \text{ cm}^3 \text{ mole}^{-1} \cdot \text{sec}^{-1}$. The reactant distribution is $\text{H}_2 + \text{I}_2$ (bound), 42%; $\text{H}_2 + \text{I}_2$ (quasibound), 13%; $\text{H}_2 + 2\text{I}$, 45%.

Reactant energy is found concentrated primarily in the I_2 vibration or dissociation and, to a lesser extent, in the H_2 translation. For reaction through sections A and B the internal energy of the iodine pairs ranges from 2.5 kcal/mole below the dissociation limit to 11 kcal/mole above. The distribution is strongly peaked in the interval from 1 kcal/mole below the limit to 2 kcal/mole above. For reaction through sections D and E the I_2 molecules are vibrationally excited in the range 5-30 kcal/mole, peaked at about 20 kcal/mole. Product HI molecules are found vibrationally excited, averaging about 20 kcal/mole.

Examination of individual trajectories reveals reaction of vibrationally excited I_2 molecules through a nearly collinear configuration. With the I_2 molecule stretched to an internuclear distance of about 5 Å, the H_2 molecule approaches from the side and inserts between the two I atoms. The H atoms separate and as the I atoms pull apart one H atom goes with each. Reactions of unbound I atom pairs and quasibound I_2 occur in a similar fashion.

IODINE ATOM PAIRS AT EQUILIBRIUM

Since there is little (average) difference between bound, quasibound, and unbound I-atom pairs with the 4.5-5.5 Å internuclear distance favorable for reaction, it is of interest to compare the availability of these pairs in an equilibrium system. From the classical partition functions^{10,17} for the three types of $^1\Sigma$ pairs, limited to internuclear distances of 4.5-5.5 Å, the relative concentrations of reactive I_2 (b), I_2 (qb), and (I+I) are estimated to be in the ratio 1.0/0.1/0.2 at 300 °K and in the

TABLE II. Conversion coefficients and reactant distributions.

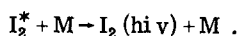
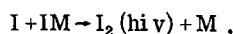
Section	Number of trajectories		Reactant distribution		
	Trials	Successes	$\text{H}_2 + \text{I}_2^b$	$\text{H}_2 + \text{I}_2^{\text{qb}}$	$\text{H}_2 + 2\text{I}$
A	228	85	18	10	57
B	168	67	39	12	16
D	27	7	7	0	0
E	7	4	4	0	0
Total	430	163	68	22	73

ratio 1.0/0.3/1.6 at 700 °K. Thus, we could expect the reaction of I_2 (b) to be strongly favored at 300 °K and a significant contributor at 700 °K.

COMPARISON WITH SULLIVAN'S EXPERIMENTS

For Sullivan's experiments the conclusion that the over-all reaction occurs by Reactions (2), (3), and/or (4) and not by the bimolecular reaction (5) requires that the relaxation of vibrationally excited I_2 (hi v) formed in recombination be rapid compared to the recombination itself. However, if relaxation of the higher levels is slow compared to recombination, then I_2 (hi v) may be at or near equilibrium with I atoms. In this case Reactions (2)–(5) are kinetically indistinguishable in Sullivan's experiments. The relative rates of recombination and relaxation in such systems have been the subject of controversy,¹⁸ and evidence that the relaxation is fast (or slow) is not conclusive.

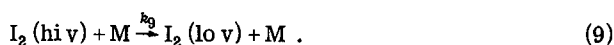
The recombination of I atoms in the presence of added gases M (M is I_2 , H_2 , He, Ar, Kr, Xe, and others) has been examined in a number of experiments.¹⁸ In the range 300–700 °K the third body I_2 is found to be several hundred times as efficient as H_2 in promoting recombination. For the concentration ratios H_2/I_2 used by Sullivan recombination with I_2 as the third body probably predominates. It is generally believed that recombination occurs by one or more of the following processes, each likely to produce vibrationally excited iodine molecules:



Each of these processes results in the over-all reaction,



which is followed by vibrational relaxation of I_2 (hi v) to a low vibrational level I_2 (lo v),



The over-all process may be written as a single reaction,



with an over-all rate constant k_{10} .

At steady state the concentration of I_2 (hi v) is given by $k_7 [I]^2 / (k_8 + k_9)$. For equilibrium with I atoms the concentration is given by $K_{78} [I]^2$ in which the equilibrium constant $K_{78} = k_7 / k_8$. The ratio γ of the steady-state concentration of I_2 (hi v) to that for equilibrium with I atoms is given by

$$\gamma = \frac{[I_2 \text{ (hi v)}]}{[I_2 \text{ (hi v)}]_{\text{equil}}} = \frac{k_8}{k_8 + k_9} = \frac{k_{10}}{K_{78} k_9}. \quad (11)$$

If relaxation is fast relative to recombination we have $\gamma = 0$ and if slow we have $\gamma = 1$.

The ratio γ is equal to the probability that a newly formed molecule I_2 (hi v) will dissociate in subsequent collisions with M before being stabilized to I_2 (lo v). As such it is equivalent to the quantity $(1 - f)$, where f is the redissociation correction factor which has been estimated by Wong and Burns¹⁹ in trajectory calculations for I-atom recombination in the presence of He, Ar, and Xe. From these calculations γ is estimated to be 0.20–0.60 depending on the mass of M as well as the temperature.

The ratio γ may also be estimated from experimental measurements of k_8 , a calculation of K_{78} , and an estimate of k_9 . At 423 °K Ip and Burns²⁰ found $k_{10} = 2.4 \times 10^{11}$ liters² mole⁻² · sec⁻¹ for $M = I_2$. Based on I_2 (hi v) in the energy range 0–4 kcal/mole below the dissociation limit, the classical partition functions for I and I_2 (hi v) give $K_{78} = 1.7$ liter mole⁻¹ at 423 °K.¹⁷ An upper limit to k_9 for $M = I_2$ is estimated as the rate constant for collisions at a cross section of 100 Å² or $k_9 = 2.3 \times 10^{11}$ liter mole⁻¹ · sec⁻¹. From Eq. (11) a lower limit for γ is estimated to be 0.6.

These estimates suggest that vibrational relaxation may not be fast with respect to I-atom recombination and that I_2 (hi v) may be present at or near equilibrium with I atoms when I_2 is the third body for recombination. Despite a large number of experiments in I-atom recombination, existing data are inadequate to resolve the question.

Sullivan's experimental results, interpreted in terms of the termolecular mechanism, yield ratios of the recombination rate constants $k_{10} (M = I_2) / k_{10} (M = H_2)$ in very good agreement with those from direct measurements of recombination rates by Bunker and Davidson²¹ and Engleman and Davidson.²² The relatively high rates of relaxation of I_2 in the $B^3\Pi$ state in collisions with H_2 as measured by Steinfeld and Klemperer²³ suggest relaxation is rapid compared to recombination for $M = H_2$. If this is the case, there seems to be no alternative to the termolecular mechanism in interpreting Sullivan's results. On the other hand, the trajectory calculations by Wong and Burns¹⁹ for recombination and relaxation with $M = \text{He}$, which gives recombination rates¹⁸ and relaxation rates²³ similar to those for $M = H_2$, indicate a value for γ of 0.70 resulting in I_2 (hi v) near equilibrium with (I+I).

A further possibility is that with I_2 as the third body for recombination the intermediate IM or I_3 fails to produce I_2 (hi v) in Reaction (7b). As shown by Bunker and Davidson²⁴ the intermediate I_3 is probably chemically bound with a heat of formation of -5.3 kcal/mole. The energy released to newly formed I_2 in Reaction (7b) might then be considerably less than the dissociation energy of I_2 . Although complicated by the electronic degeneracy of I atoms this question might be clarified by additional trajectory calculations if the results are insensitive to variations in the potential energy surfaces used.

CONCLUSIONS

The trajectory calculations reported here suggest the over-all reaction of hydrogen with iodine occurs by both bimolecular and termolecular mechanisms. Consideration of the availability of reactive I-atom pairs in thermal systems suggests the bimolecular reaction is strongly favored at 300 °K and a major contributor at 700 °K.

Although Sullivan's experiments have eliminated the possibility of a significant contribution by the bimolecular reaction involving I_2 in low or intermediate states of vibrational excitation, the possibility of a large contribution by the bimolecular reaction of I_2 excited near the dissociation limit remains open. The present knowledge of the I-atom recombination is inadequate for resolution of the question. While the trajectory calculations show the bimolecular and termolecular reactions have nearly equal importance at 700 °K, slight variations in the potential energy surface used could probably tip the balance either way. Still, Nature, in her wonderful perversity, might well have made the reaction half-bimolecular, half-termolecular.

¹J. H. Sullivan, *J. Chem. Phys.* 46, 73 (1967).

²We use the term (I+I) for I-atom pairs with internal energy greater than the dissociation energy which are not trapped by the rotational barrier to dissociation. Quasibound pairs $I_2(qb)$ have internal energy greater than the dissociation energy and are trapped within the rotational barrier. Sullivan's I_2^* includes both (I+I) and $I_2(qb)$. Bound I_2 molecules with internal energies less than the dissociation energy are identified by I_2 or $I_2(b)$ and more specific terms: $I_2(hi v)$, $I_2(lo v)$.

³L. C. Cusachs, M. Krieger, and C. W. McCurdy, *J. Chem. Phys.* 49, 3740 (1968).

⁴F. L. Minn and A. B. Hanratty, *J. Chem. Phys.* 53, 2543 (1970); *Theoret. Chim. Acta* 19, 390 (1970).

⁵R. Hoffmann, *J. Chem. Phys.* 49, 3739 (1968).

⁶R. N. Porter and L. M. Raff, *J. Chem. Phys.* 50, 5216 (1969).

⁷L. M. Raff and R. N. Porter, *J. Chem. Phys.* 51, 4701 (1969).

⁸L. M. Raff, L. Stivers, R. N. Porter, D. L. Thompson, and L. B. Sims, *J. Chem. Phys.* 52, 3449 (1970).

⁹L. M. Raff, D. L. Thompson, L. B. Sims, and R. N. Porter, *J. Chem. Phys.* 56, 5998 (1972).

¹⁰R. L. Jaffe, J. M. Henry, and J. B. Anderson, "Molecular Dynamics of the Hydrogen Iodide and Hydrogen-Iodine Exchange Reactions" (unpublished).

¹¹J. M. Henry, R. L. Jaffe, and J. B. Anderson, *Chem. Phys. Lett.* 20, 138 (1973).

¹²J. B. Anderson, J. M. Henry, and R. L. Jaffe, *J. Chem. Phys.* 60, 3725 (1974).

¹³J. B. Anderson and R. T. V. Kung, *J. Chem. Phys.* 58, 2477 (1973); 60, 2202 (1974).

¹⁴R. N. Porter, D. L. Thompson, L. M. Raff, and J. M. White, "Comparison of the Combined Phase-Space Trajectory and Quasiclassical Trajectory Methods in the Study of Reaction Dynamics: $H+I_2$ and $H+Br_2$," *J. Chem. Phys.* (to be published).

¹⁵J. D. McDonald, P. R. Le Breton, Y. T. Lee, and D. R. Herschbach, *J. Chem. Phys.* 56, 769 (1972).

¹⁶Y. T. Lee (private communication, 1974).

¹⁷The reactive pairs (I+I) include only those in the $^1\Sigma$ electronic state, approximately 1/16 of the total.

¹⁸For reviews, see (a) D. L. Bunker, *Theory of Elementary Gas Reaction Rates* (Pergamon, Oxford, England, 1966), p. 76ff; (b) H. S. Johnston, *Gas Phase Reaction Rate Theory* (Ronald Press, New York, 1966), p. 253 ff.

¹⁹W. H. Wong and G. Burns, *J. Chem. Phys.* 58, 4459 (1973).

²⁰J. K. K. Ip and G. Burns, *J. Chem. Phys.* 56, 3155 (1972).

²¹D. L. Bunker and N. Davidson, *J. Am. Chem. Soc.* 80, 5085 (1958).

²²R. Engleman and N. Davidson, *J. Am. Chem. Soc.* 82, 4770 (1960).

²³J. I. Steinfeld and W. Klemperer, *J. Chem. Phys.* 42, 3475 (1965).

²⁴D. L. Bunker and N. Davidson, *J. Am. Chem. Soc.* 80, 5090 (1958).