

# Hydrogen Iodide Revisited. Continued Significance of the Sullivan Experiments

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**Abstract:** We are in agreement with Hammes and Widom that hydrogen molecules may in principle react either with previously separated iodine atoms or with highly excited iodine molecules in states whose populations are in equilibrium with free atoms even in photostationary systems. We agree also that theoretical chemistry cannot yet unequivocally determine whether excited iodine molecules or previously separated atoms react preferentially with hydrogen molecules. However, we believe experimental rate constants for iodine atom recombination and theoretical efforts to model the recombination process both make it very unlikely that excited molecular states do in fact contribute significantly to the rate of hydrogen iodide formation. Even if the excited states proposed by Hammes and Widom are indeed mechanistically significant, the Sullivan experiments still demonstrate that only a very limited number of molecular states of iodine are capable of reacting with hydrogen. They further demonstrate that statistical methods based on temperature and total energy of the molecular system are not of themselves sufficient to calculate chemical reactivity; the prior state of a reactant species is also a necessary piece of information.

As Hammes and Widom<sup>1</sup> correctly point out, the Sullivan<sup>2</sup> photochemical experiments demonstrate that hydrogen iodide is formed only when a hydrogen molecule reacts either with a previously separated pair of iodine atoms or with an iodine molecule in an excited state whose population is in equilibrium with separated atoms; the experiments do not of themselves determine the relative contributions from these alternative mechanisms.

Hammes and Widom<sup>1</sup> further assert that model calculations are incapable of determining whether atom pairs or excited molecules will react preferentially with hydrogen and are also incapable of demonstrating the presence or absence of excited molecular iodine states in equilibrium with photochemically generated atoms. They conclude that because of these ambiguities the Sullivan<sup>2</sup> experiments do not distinguish the relative importance of molecular and atom-pair mechanisms to the synthesis of hydrogen iodide.

The argument of Hammes and Widom<sup>1</sup> can only be valid if there are indeed highly excited but bound states of iodine molecules that are more likely to be dissociated than to be stabilized by random collisions with other molecules. If a molecule contains very much more than  $kT$  of energy in one of its modes of motion, the Boltzmann H theorem<sup>3</sup> and the second law of thermodynamics indicate such a molecule is generally more apt to lose energy than to gain it as a result of random interactions with thermally equilibrated species. The unusual states proposed by Hammes and Widom<sup>1</sup> are not absolutely precluded by theory, but they must certainly be a very small fraction of the total of excited states of molecular iodine. We shall argue below that both experimental observations and model calculations on iodine-atom recombination make it very doubtful that a significant fraction of recombinations proceed through molecular states whose populations are in equilibrium with separated atoms. In conclusion, we shall argue that even if such states do exist the Sullivan<sup>2</sup> observations nevertheless provide significant and previously unanticipated mechanistic information.

**Evidence Based on Absolute Rates of Atom Recombination.** It is well established that iodine atom recombination is a third-order process. The rate at which separated atoms form stable molecules is given by eq 1 where X is a specific

$$d[I_2]/dt = k_X[I]^2[X] \quad (1)$$

molecular species.

In order to develop a very crude model of the recombina-

tion, let  $[2I]_r$  be the concentration of pairs of freely moving atoms whose centers are momentarily within a sphere of radius  $r$ . At these low atom concentrations, we may approximate  $[2I]_r$  by eq 2. This approximation will actually be

$$[2I]_r = \frac{4}{3}\pi r^2 [I]^2 \quad (2)$$

somewhat too large because presence of one atom in a sphere physically excludes part of the volume to the second atom.

We may use conventional collision theory to calculate the rate at which spheres of radius  $r$  containing two free iodine atoms will collide with molecules having molecular weight  $M_X$  and radius  $\Delta_X$ .

Finally, let  $\alpha$  be the probability such a collision forms an excited molecular iodine species that is subsequently stabilized by additional collisions. Of course  $\alpha$  must be less than unity. If collisions can produce excited molecular species that are in equilibrium with free atoms as proposed by Hammes and Widom,<sup>1</sup> those species must be more likely to dissociate than to be stabilized by subsequent events. If the Hammes and Widom<sup>1</sup> model is to be correct, then  $\alpha$  can hardly be greater than 0.1.

If this model is applied to eq 1, we obtain eq 3.

$$k_X = (8\pi RT)^{1/2} \left( \frac{1}{M_{2I}} + \frac{1}{M_X} \right)^{1/2} (r + \Delta_X)^2 \frac{4}{3}\pi r^2 \alpha \quad (3)$$

Sullivan<sup>2</sup> did photochemical measurements at three temperatures, the middle one being 480.7°K. At this temperature, he used values of  $k_{H_2} = 2.37 \times 10^9 \text{ l}^2 \text{ mol}^{-2} \text{ sec}^{-1} = 6.53 \times 10^{-33} \text{ ml}^2 \text{ molecule}^{-2} \text{ sec}^{-1}$  and  $k_{I_2} = 1.235 \times 10^{11} \text{ l}^2 \text{ mol}^{-2} \text{ sec}^{-1} = 3.405 \times 10^{-31} \text{ ml}^2 \text{ molecule}^{-2} \text{ sec}^{-1}$ . For most of his experiments at this temperature, iodine molecules contributed much more than hydrogen molecules to the rate of atom recombination. If these values are substituted into eq 3, we obtain

$$\alpha r^2 (r + \Delta_{H_2})^2 = 22.0 \text{ \AA}^5 \text{ for } H_2$$

$$\alpha r^2 (r + \Delta_{I_2})^2 = 9140 \text{ \AA}^5 \text{ for } I_2$$

A value of  $\Delta_{H_2} = 1.09 \text{ \AA}$  has been estimated from gas viscosity measurements.<sup>4</sup> The comparable value for chlorine molecules is 1.85 Å, and we shall estimate  $\Delta_{I_2} = 2.5 \text{ \AA}$ . Then for X = H<sub>2</sub>,  $r = 1.49 \text{ \AA}$  if  $\alpha = 1$  and  $r = 2.55 \text{ \AA}$  if  $\alpha = 0.1$ . For X = I<sub>2</sub>,  $r = 5.3 \text{ \AA}$  if  $\alpha = 1$  and  $r = 8.9 \text{ \AA}$  if  $\alpha =$

0.1. In crystalline elementary iodine, centers of atoms from different molecules are 4.3 Å apart at contact.

Hydrogen is rather inefficient at promoting iodine atom recombination, and the data for this substance are not in conflict with the model proposed by Hammes and Widom.<sup>1</sup> However, molecular iodine is extremely efficient at promoting recombination. It is barely possible to fit this model to the data even if  $\alpha$  is unity, and it appears virtually impossible to accommodate the experimental observations if  $\alpha$  is to be small enough that the initial excited molecules have a high probability of redissociation.

**Other Attempts to Model Atom Recombination.** Recombination of free atoms is a sufficiently simple process that there can be some confidence in efforts at theoretical modeling. Hammes and Widom<sup>1</sup> refer to the calculations of Wong and Burns<sup>5</sup> which indicate that up to 60% of the excited iodine molecules initially formed may be dissociated by subsequent collisions without becoming stabilized. However, if Hammes and Widom<sup>1</sup> are to explain the Sullivan<sup>2</sup> observations by excited molecules equilibrated with free atoms, a figure of 90% dissociation would be more appropriate. It should also be pointed out that Wong and Burns<sup>5</sup> get large fractions of redissociation only for light monatomic species like helium at rather high temperatures; the Sullivan experiments contained considerable numbers of iodine molecules for which stabilization is almost certainly more efficient relative to dissociation than it is for helium.

Johnston and Birks<sup>6</sup> attempted to model iodine molecule dissociation rates over a very wide range of temperature and obtained quite satisfactory agreement with experimental observations. Their conclusions are pertinent to the reverse process of atom recombination. At temperatures above 1000° K, they calculate an apparent activation energy significantly less than the bond dissociation energy and therefore predict the existence of highly excited states which are more likely to dissociate to atoms than to be stabilized, just as Hammes and Widom<sup>1</sup> have proposed. However, the very successful model of Johnston and Birks<sup>6</sup> does not predict any significant equilibration of atoms and excited molecules at temperatures near 500° K where Sullivan<sup>2</sup> made his measurements.

We are not aware of any theoretical effort to model the quantitative recombination of iodine atoms that predicts there should be significant redissociation of excited molecules in a system near 500° K and containing a considerable concentration of iodine molecules.

**Concluding Comments.** The above attempts to examine the system quantitatively make it appear very doubtful to us that the Sullivan<sup>2</sup> photochemical system contained any significant populations of excited molecules that were destined to redissociate and could therefore be considered in equilibrium with free atoms. We doubt that such species could have made a major contribution to the production of hydrogen iodide. However, we wish to assert that even if such excited molecules were present, and even if they were responsible for much or all of the hydrogen iodide formation observed by Sullivan,<sup>2</sup> his experimental observations were still

unanticipated and of major mechanistic importance.

As was pointed out in the introductory section, arguments based on statistical thermodynamics require that most of the many excited states of iodine molecules could not possibly be in equilibrium with a photostationary concentration of free iodine atoms. The great significance of the Sullivan<sup>2</sup> observations is the unequivocal demonstration that these unequilibrated excited states do not contribute significantly to the elementary processes that produce hydrogen iodide.

It is the Sullivan<sup>2</sup> interpretation that hydrogen iodide formation requires two previously separated iodine atoms. It is the interpretation of Hammes and Widom<sup>1</sup> that a very few highly excited states of iodine molecules could also be responsible for the observed reaction. It is almost (but not quite) a semantic quibble to distinguish between reaction by a free pair of atoms and reaction by a molecule so excited it would almost certainly dissociate during any collision that did not cause it to react. The Hammes and Widom<sup>1</sup> interpretation raises the serious question as to why so very few of the many possible excited molecular states can react with hydrogen.

It has been popular to interpret chemical processes in terms of motion along a reaction coordinate.<sup>7</sup> It is assumed that excitation of other normal coordinates can be calculated by standard statistical procedures. The Sullivan<sup>2</sup> experiments demonstrate that such an interpretation is *not* a satisfactory description of this particular chemical system.<sup>8</sup> The probability a hydrogen molecule will react during a particular encounter is determined not by the total energy of the molecular system but by the specific initial state of the pair of iodine atoms involved. It matters little whether those iodine atoms were initially free as claimed by Sullivan<sup>2</sup> and by Noyes<sup>8</sup> or were in a very specific excited molecular state as claimed by Hammes and Widom;<sup>1</sup> the prediction of reactivity requires information about prior history of the molecular system and cannot possibly be inferred by statistical methods that consider only the total energy of the transition state. This conclusion was the major unanticipated consequence of the Sullivan<sup>2</sup> experiments.

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## References and Notes

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