On the Mechanism of the Hydrogen–Iodine Reaction

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Abstract: An analysis of the reaction between hydrogen and iodine is presented. The proposal is advanced that in the photochemical production of HI from H_2 and I_2, the absorption of light may increase the concentration of the most reactive iodine molecules in the same proportion as it increases the square of the concentration of iodine atoms. This is due to the possibility of the reactive molecules being in mobile equilibrium with the atoms. If this is the case, the two mechanisms $H_2 + I_2 \rightarrow 2HI$ and $H_2 + 2I \rightarrow 2HI$ have not yet been distinguished by experiment.

The question has frequently been raised whether the gasphase reaction

$$H_2 + I_2 \longrightarrow 2HI \qquad (1)$$

(at temperatures below that at which an atomic chain mechanism becomes important) proceeds as written, as a bimolecular reaction of hydrogen with molecular iodine, or proceeds instead as a termolecular reaction of hydrogen with atomic iodine.

$$H_2 + 2I \longrightarrow 2HI \qquad (2)$$
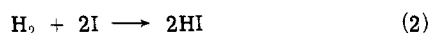
An important experiment by Sullivan[1] has been widely quoted as demonstrating that the reaction mechanism is (2) not (1).[2] We point out here that the argument leading to this conclusion depends in an essential way on an assumption that has little experimental or theoretical support and may in fact not be correct. We conclude that the two routes (reactions 1 and 2) are still kinetically indistinguishable.

In the thermal reaction the concentration [I] of iodine atoms is much less than the concentration $[I_2]$ of iodine molecules, and one measures a rate constant k^{th} defined by

$$\text{rate} = k^{th}[H_2][I_2] \qquad \text{(thermal reaction)} \qquad (3)$$

In the photostationary-state reaction[1] the temperature is so low that the right-hand side of (3) would be immeasurably small, yet the reaction rate is appreciable due to a high concentration of iodine atoms that are continuously produced by photodissociation of I_2. In this reaction one measures a rate constant k^{ph} defined by

$$\text{rate} = k^{ph}[H_2][I]^2 \qquad \text{(photostationary-state reaction)} \qquad (4)$$

When they are extrapolated to a common temperature, k^{th} and k^{ph} are found[1] to be related by

$$k^{th} = Kk^{ph} \qquad (5)$$

where K is the equilibrium constant for the iodine dissociation $I_2 \rightleftarrows 2I$ at that temperature. The relation 5, which holds within the small uncertainties in the measurement, is the central experimental fact.

The conclusion that (1) contributes negligibly to the thermal reaction, and therefore that the reaction occurs *via* the mechanism in (2), is often thought to be a consequence of (5), apparently by the following argument. Let k_1 and k_2 be the rate constants for reactions 1 and 2. Recognizing that I and I_2 are in mobile equilibrium during the course of the thermal reaction, we have

$$k^{th} = k_1 + Kk_2 \qquad (6)$$

Then, if it is supposed that the quantity measured as k^{ph} in

the photostationary-state reaction is k_2, it follows from (5) and (6) that $k_1 = 0$ and that the whole of kth is just Kk_2.

The identification of k^{ph} with k_2 is based on the assumption that the only effect of the absorption of light in the photostationary state is to increase greatly the concentration of iodine atoms, *without* correspondingly increasing the concentration of the most reactive of the molecular I_2. This seems improbable, for the following reason. Represent the reactive molecular species by I_2^*, which may be thought of as iodine molecules in their ground electronic states with appropriate degrees of vibrational and rotational excitation, perhaps (as is likely) near their dissociation limits. This reactive species can be imagined formed from 2I by atomic recombination, which is in any case much faster than the reaction with H_2. If, now, the rate of the redissociation $I_2^* \rightarrow 2I$ is greater than that of the deexcitation $I_2^* \rightarrow I_2$ (this is a crucial point, to which we return presently), then the factor by which $[I_2^*]/[I_2]$ in the photostationary state exceeds its thermal value is identical with the factor by which $[I]^2/[I_2]$ exceeds its thermal value. This may be seen from the reaction scheme

$$2I \underset{k_3}{\overset{}{\rightleftharpoons}} I_2^* \overset{k_4}{\rightleftharpoons} I_2 \qquad (7)$$
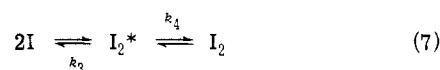
We now assume the thermal reaction with H_2 to be slow enough so that during its course $[I]^2/[I_2]$ and $[I_2^*]/[I_2]$ have their equilibrium values, from which it follows that if $[I]^2/[I_2]$ in the photostationary state is greater by the factor x than it is in the thermal reaction, and $[I_2^*]/[I_2]$ is greater by the factor y, then

$$y = (k_4 + k_3x)/(k_4 + k_3) \qquad (8)$$

so $y = x$ when $k_3 \gg k_4$, as stated.

The significance of the enhancement of $[I_2^*]/[I_2]$ in the photostationary state being the same as that of $[I]^2/[I_2]$ is the following. Let x be the common value of the enhancement factor. Then the net rate of the photochemical reaction is

$$\text{rate} = [xk_1[I_2] + k_2[I]^2][H_2] \qquad \text{(photostationary-state reaction)} \qquad (9)$$

while at the same time

$$[I]^2/[I_2] = xK \qquad \text{(photostationary-state reaction)} \qquad (10)$$

Thus, from (4)

$$k^{ph} = K^{-1}k_1 + k_2 \qquad (11)$$

rather than $k^{ph} = k_2$. The experimental result (5), therefore, could have been *predicted* by eq 6 and 11 of this anal-

ysis. When the assumption $k^{ph} = k_2$ is replaced by eq 11, it is no longer possible to draw from (5) and (6) any conclusion about the relative magnitudes of k_1 and Kk_2; that is, (1) and (2) remain kinetically indistinguishable. It is essential to this argument that the redissociation of I_2^* be faster than its deexcitation, so that the absorbed light in the photostationary-state experiment increases the reactivity of the molecular species in the same proportion as it increases $[I]^2/[I_2]$. There is no direct experimental evidence to settle this point. As long as it remains a possibility, the photochemical experiment is unable to distinguish mechanisms 1 and 2.

A second important observation made by Sullivan,[1] in addition to relation 5, is that the iodine species that reacts in the photochemical production of HI is (or, what amounts to the same thing, is in mobile equilibrium with) the species that reacts in the rate-determining step of iodine-atom recombination. Then our picture that I_2^* and $2I$ are rapidly equilibrated and thus act as a single, kinetically undifferentiated species in the reaction with H_2 would imply that the same I_2^* and $2I$ are also the species that react in the rate-determining step of the recombination reaction. The separate, direct contributions to these reactions that are made by the molecules in each microscopic rotation–vibration state of I_2^* or in each translational- and angular-momentum state of atom pairs $2I$ may well vary from one of these reactions to the other, being different in the reaction that forms HI from what it is in the iodine-atom recombination reaction, and, in the latter case, even depending on whether the recombination occurs with H_2 or with I_2 as the collision partner, but so long as the populations in these states are rapidly equilibrated among each other, they will behave, kinetically, as a single entity, and no distinction among them will be possible. The microscopic states in question may be those that are within a few kT of the I_2 dissociation limit, on either side of it; however, this is just a guess, as no *experimental* evidence on that exists at present.

Whether (1) or (2) is the mechanism of the hydrogen-iodine reaction also cannot be deduced theoretically. One set of dynamical calculations[3] indicates that (2) is the mechanism, but this is contradicted by other calculations[4] with the identical potential surface. In any case, the outcome of the calculations depends sensitively on the details of the potential surface, and there is serious doubt about whether the one used in those studies was correct.[5]

The kinetic equivalence of I_2^* and $2I$ depends on the assumption that, in the I_2–H_2 mixture, the redissociation of I_2^* is faster than its deexcitation. Here, too, the theoretical evidence is inconclusive. The most recent calculations[6] indicate that with *inert gas atoms* as third bodies, almost all of the I_2 molecules that are first formed in recombination are of energy within a few kT of the dissociation limit, and that, depending on the temperature and on the identity of the inert gas, anywhere from 20 to 60% of these redissociate before they are deexcited.

It has been suggested[7] that a significant route in the recombination of *hydrogen* atoms may be one in which the rate-determining step is the deexcitation of a "quasi-bound" H_2^*, that is, an H_2^* of total energy greater than the dissociation energy but trapped by a centrifugal barrier. Whether such a state is really one of H_2 or of $2H$, and therefore whether this mechanism is molecular or atomic, appears to be an artificial distinction. Similarly, if the reaction of quasi-bound I_2^* with H_2 contributes significantly to the hydrogen-iodine reaction, then not only have (1) and (2) not yet been distinguished by experiment, but it is not apparent that a meaningful distinction exists.

It would obviously be of great value in helping to decide these and other questions to be able to monitor the populations of highly excited rotation–vibration states of I_2 during the course of the atomic recombination reaction. This might perhaps be feasible by laser spectroscopy.

References and Notes

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