

## Transition State for the Hydrogen–Iodine and the Hydrogen Exchange Reactions

Roald Hoffmann

Citation: *J. Chem. Phys.* **49**, 3739 (1968); doi: 10.1063/1.1670671

View online: <http://dx.doi.org/10.1063/1.1670671>

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served at  $3490\text{ cm}^{-1}$ . This band was replaced by a band at  $2580\text{ cm}^{-1}$  when the sample was heated at  $750^\circ\text{C}$  in an atmosphere of heavy water as shown in the accompanying Fig. 1(a). The heat treatment was done by placing the sample in a vented tube which contained heavy water. The tube was heated in a tube furnace where the sample was placed in the center and water was placed in a cooler region. To see if the  $\text{D}^+$  replacing the  $\text{H}^+$  was reversible, the sample was heated in an atmosphere saturated with water at  $500^\circ\text{C}$  for 40 min. The OH band at  $3490\text{ cm}^{-1}$  reappeared, and the magnitude of the OD band decreased as shown in Fig. 1(b). The OD band disappeared completely when the sample was heated at  $700^\circ\text{C}$  for 30 min. in a humid atmosphere as shown in Fig. 1(c). It seems that deuterium and hydrogen replace each other in these crystals. It was found also that the magnitude of the OH band changed when the sample was heated in air, pointing out the ease with which  $\text{H}^+$  moves in the crystal. The magnitude of the OH band did not decrease when the sample was repolished on both sides. This shows that the  $\text{H}^+$  is in the bulk of the crystal.

Additional evidence that these two absorption bands have been correctly assigned to OH and OD stretching vibrations is obtained from the value of the ratio of their vibrational frequencies. The observed value ( $\nu_{\text{H}}/\nu_{\text{D}}=1.35$ ) is very close to the expected value of 1.37 which is computed from the reduced masses, assuming the vibrational frequency is inversely proportional to the square root of the reduced mass. The experimental value of 1.35 in  $\text{SrTiO}_3$  is identical to the value in  $\text{TiO}_2$  reported by Soffer.<sup>1</sup>

Johnson<sup>2</sup> has proposed a model for  $\text{H}^+$  in  $\text{TiO}_2$  single crystals. He suggests that an impurity complex is formed consisting of  $\text{H}^+$  or  $\text{D}^+$  between two oxygen ions in normal lattice sites adjacent to a substitutional impurity of valence  $3+$ , such as  $\text{Fe}^{3+}$  or  $\text{Al}^{3+}$ . It seems likely that  $\text{H}^+$  and  $\text{D}^+$  replace each other in centers adjacent to impurity ions.

The displacement ( $\Delta\nu$ ) of the OH stretching vibration frequency from the known nonbonded value of  $3700\text{ cm}^{-1}$  can be correlated to the O-O distance of the competing oxygen ions in the crystal. Pimentel *et al.*<sup>3</sup> determined a quantitative relation between  $\Delta\nu$  and the O-O distance. From the observed value of  $3490\text{ cm}^{-1}$  one finds using their relation that the O-O distance is about  $2.82\text{ \AA}$ . In  $\text{SrTiO}_3$  the neighboring oxygen ions in normal lattice sites are equidistant from each other at a distance of  $2.76\text{ \AA}$ .<sup>4</sup>

The suggestions of Dr. R. R. Addiss and the experimental assistance of B. Perkins, L. Thibault, and J. P. Sachse are greatly appreciated.

<sup>1</sup> B. H. Soffer, *J. Chem. Phys.* **35**, 940 (1961).

<sup>2</sup> O. W. Johnson, *Bull. Am. Phys. Soc.* **12**, 932 (1967).

<sup>3</sup> G. C. Pimentel and A. L. McClellan, *The Hydrogen Bond* (W. H. Freeman and Co., San Francisco, Calif., 1960).

<sup>4</sup> H. D. Megaw, *Proc. Phys. Soc. (London)* **58**, 133 (1946)

## Comments

### Transition State for the Hydrogen-Iodine and the Hydrogen Exchange Reactions

ROALD HOFFMANN

*Department of Chemistry, Cornell University, Ithaca, New York*

(Received 18 March 1968)

There has recently appeared a provocative discussion of the hydrogen-iodine reaction.<sup>1</sup> In examining the possible geometries of the transition state for the hypothetical molecular reaction, the above discussion presents some arguments as well as a personal conviction that the "trapezoidal" structure will be more stable than other arrangements, such as the linear and staggered structures. This supposition has a long history. I would like to present some simple quantum-mechanical arguments which suggest that the trapezoidal geometry should be branded energetically unlikely, and similarly, that a square  $D_{4h}$  transition state for the hydrogen exchange reaction should be at high energy.

Consider the construction of a level correlation diagram<sup>2</sup> for the exchange reaction  $\text{H}_2 + \text{D}_2 = 2\text{HD}$ , proceeding through the sequence of conformations  $D_{2h} \rightarrow D_{4h} \rightarrow D_{2h}$ . Only the  $\sigma_g$  and  $\sigma_u$  orbitals of each  $\text{H}_2$  molecule will be considered.

Let the molecular orbitals of the system be classified as symmetric (S) or antisymmetric (A) with respect to reflection in two perpendicular mirror planes. The  $\sigma_g$  levels of the "reactants" are clearly symmetric under reflection in Plane 1, whereas those of the "products" are symmetric under reflection in Plane 2. When the

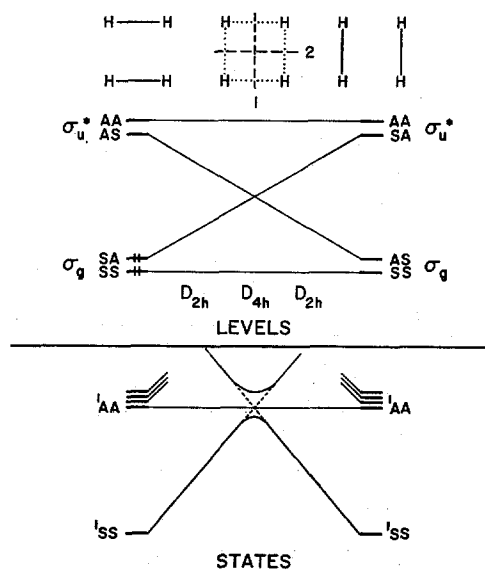


FIG. 1. Level and state correlation diagrams for the hydrogen exchange reaction.

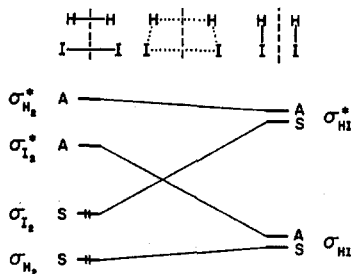


FIG. 2. Level correlation diagram for the exchange reaction for the hydrogen-iodine reaction proceeding through a trapezoidal transition state.

proper symmetry-adapted combinations are formed, the construction of the correlation diagram follows trivially (Fig. 1).

This correlation diagram obviously resembles that for the cycloaddition of ethylene to ethylene and is characteristic of a thermally forbidden and photochemically allowed reaction.<sup>3,4</sup> In simple terms, the concerted exchange reaction proceeding through a  $D_{4h}$  transition state would not conserve orbital symmetry. The energy price to be paid, if the reaction were concerted, is difficult to estimate, but it should be somewhat less than the cost of promoting two bonding electrons on  $H_2$  to nonbonding, i.e., 4.7 eV. The correlation diagrams may be used to eliminate other highly symmetrical transition states, such as those of  $T_d$  or  $D_{6h}$  geometry. But they cannot predict the preferred geometry among the many choices of low symmetry. Some approximate molecular-orbital calculations we have done indicate (1) a preference for a colinear approach at large  $H_2-H_2$  separation, (2) energetically favored distortion of the  $D_{4h}$  geometry to a  $C_{2v}$  "kite" shape. Much better calculations of the  $H_2-H_2$  potential surface are still ambiguous about the topology of the surface.<sup>5</sup>

The correlation diagram for the  $H_2+I_2$  reaction proceeding through a trapezoidal transition state is just as simple to draw (Fig. 2). The element of symmetry maintained is a plane bisecting reactants  $H_2$  and  $I_2$ .<sup>6</sup> The ground-state reaction is once again symmetry forbidden. The correlation diagrams indicate that the reaction should not be concerted (through a trapezoidal transition state) but give again no information on which of the less symmetrical geometries should be preferred. To specify these, some detailed calculations are needed.

Our simple arguments cannot account for the apparently very low energies of activation observed for the reactions of  $I_2$  and  $Br_2$ ,<sup>7</sup> and  $Br_2$  and  $Cl_2$ .<sup>8</sup> There is yet no agreement on the vapor-phase homogeneity of these reactions.<sup>9</sup>

I would like to thank S. H. Bauer and B. Widom for many discussions on this topic.

<sup>1</sup> R. M. Noyes, *J. Chem. Phys.* **48**, 323 (1968).

<sup>2</sup> R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.* **87**, 2046 (1965); H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.* **87**, 2045 (1965).

<sup>3</sup> R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.* **87**, 395, 2511 (1965); R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.* **1**, 17 (1968).

<sup>4</sup> Such correlation diagrams for the exchange reaction have been constructed previously, but were not correctly interpreted. See V. Griffing, *J. Chem. Phys.* **23**, 1015 (1955); *J. Phys. Chem.* **61**, 11 (1957).

<sup>5</sup> K. Morokuma, L. Pedersen, and M. Karplus, *J. Am. Chem. Soc.* **89**, 5064 (1967), particularly Ref. 7.

<sup>6</sup> Inclusion of the two lone pairs on each I atom, which have the same symmetry as the bonds made or broken, has no effect on the correlation diagram.

<sup>7</sup> P. R. Walton and R. M. Noyes, *J. Am. Chem. Soc.* **88**, 4324 (1966).

<sup>8</sup> P. R. Walton and R. M. Noyes, *J. Phys. Chem.* **71**, 1952 (1967).

<sup>9</sup> The vapor-phase reaction of  $Br_2$  and  $Cl_2$  was first studied by W. Jost, *Z. Physik. Chem.* **B14**, 413 (1931), who may have observed the analogous photochemical reaction [H. G. Vesper and G. K. Rollefson, *J. Am. Chem. Soc.* **56**, 620 (1934)]. A restudy of the system by G. Brauer and E. Victor, *Z. Elektrochem.* **41**, 508 (1935) revealed the slightly slower dark reaction, but there was evidence of heterogeneous character. Recent work by W. Wen, P. Goldfinger, and R. M. Noyes indicates a molecular process. I am grateful to R. M. Noyes for the above references.

## Mechanism of the Hydrogen-Iodine Reaction at Low Temperature

L. C. CUSACHS, M. KRIEGER, AND C. W. MCCURDY  
*Richardson Chemistry Laboratories, Tulane University,  
New Orleans, Louisiana 70118*

(Received 27 March 1968)

Recent experiments reported by Sullivan<sup>1</sup> show that the mechanism



is sufficient to account for the observed rate of the process previously supposed<sup>2</sup> to proceed directly:



Noyes<sup>3</sup> suggested that a paradox should exist in the application of kinetic theory to this process unless one of three unpleasant conditions were to hold. The first of these conditions is that "it is impossible to construct a potential-energy surface that increases monotonously (sic) as a hydrogen and an iodine molecule react to attain the transition state of the experimentally observed process leading to 2HI." This could be demonstrated by showing that the transition state of the process believed to occur is inaccessible to the simple bimolecular collision of  $H_2$  and  $I_2$  molecules. It would imply that equilibrium between  $H_2+I_2$  and 2HI cannot be reached directly by the bimolecular mechanism, at least at low temperatures, but must be mediated by iodine atoms, or a chain reaction, or other indirect processes. The heart of the matter is the question whether a low-energy path of type (2) above exists, i.e., is accessible in the statistical-mechanical sense, or is allowed in the quantum-mechanical sense. This question would be extremely difficult to answer rigorously, since it concerns regions of collision processes which may not safely be assumed to be molecules in stationary quan-