▸11◂

Reaction Mechanisms of Coordination Compounds

• •

> The chemistry of transition metal complexes involves ligand coordination to metals, exchange of ligands, coordination-sphere rearrangement, oxidation and reduction, and alteration of ligand reactivity by coordination. A thorough appreciation of complex chemistry requires a knowledge of reaction mechanisms. The relatively simple complexes discussed here serve as models displaying the main mechanistic features for coordination compounds.
>
> In this chapter we look first at the model for understanding reaction kinetics and mechanisms. Then we discuss substitution reactions of octahedral Werner complexes, developing the concepts needed for relating the model to experiment. After dealing briefly with recemization reactions of optically active octahedral complexes, we treat ligand substitution reactions of square-planar complexes. Next, the mechanisms of redox reactions are explored. Finally, a brief look is taken at photochemical reactions. Reaction mechanisms for complexes containing π-acid ligands are discussed in Chapter 14.

THE KINETIC MODEL

The model that chemists currently use to rationalize and predict what goes on during chemical reactions was developed in the 1930s from transition-state theory. The course of reactions is seen as involving collision of reactants sufficiently energetic to form the **activated complex** (or **transition state**). Along the path from reactants to products, kinetic energy is converted to potential energy by bond stretching, partial bond formation, angu-

lar distortions, and so on. The exact processes that occur depend on the particular reaction. The transition state is the species of maximum potential energy resulting from these motions. All energetically unfavorable processes have occurred by the time a transition state is reached. The energy required to reach the transition state from the reactant ground state is called the **activation energy**. After the transition state, the collection of atoms rearranges toward more stable species: old bonds are fully broken, new ones are fully made, and geometric rearrangement toward a more stable configuration (**relaxation**) occurs. In multistep reactions a new transition state is reached for each distinguishable step.

Plots can be made (at least in principle) of the energy of a reacting system as a function of relative atomic positions. As an example, consider the reaction[1] $H_2 + F \rightarrow HF + H$ when all reactants are confined to a straight line. The distances between atoms r_{H-H} and r_{H-F} describe relative atomic positions. A plot of energy versus two variables is three-dimensional. Figure 11.1a shows a two-dimensional **contour plot** representation. Lines represent the shape of the intersection of a plane having the indicated energy value with the three-dimensional energy surface. (The energy zero is the energy of $H_2 + F$.) Such a contour plot is like a terrain map showing contours of constant altitude. At very large r_{H-F} (bottom right), a cut through the plot (A–B) is just the H–H energy versus distance curve. At very large r_{H-H}, a cut through the plot (C–D) gives the H–F energy versus distance curve. Figure 11.1b shows computer-generated three-dimensional plots for the two different sections of the potential surface. At very large interatomic distances (top right of the plot), the energy is essentially independent of the distance and the surface is a plateau. Any linear collection of HHF atoms takes the lowest-energy path along the contour plot's valleys. This path (indicated by a dashed line in Figure 11.1a) involves changes in both r_{H-H} and r_{H-F}; it is called the **reaction coordinate**.
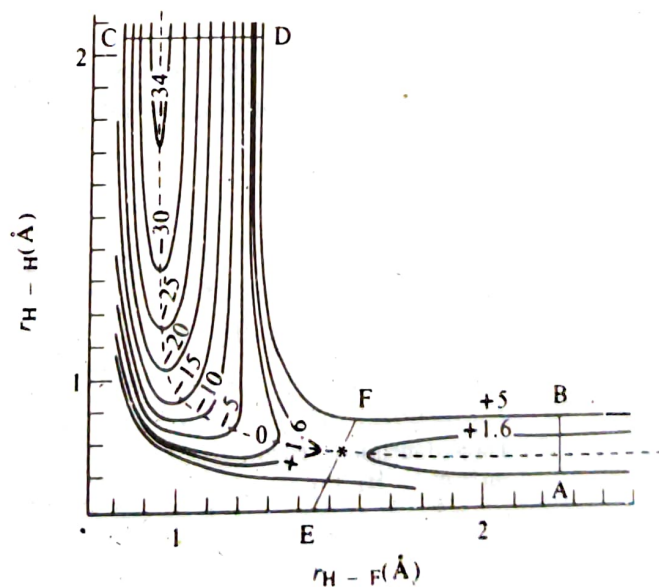
(a) Contour plot for $H_2 + F = H + HF$

Figure 11.1   Plots for the reaction $H_2 + F \rightleftarrows H + HF$. (Parts *a* and *b* are from The University of California, Lawrence Livermore National Laboratory and the Department of Energy, under whose auspices the work was performed when these figures were used; and C. F. Bender, S. V. O'Neill, P. K. Pearson, and H. F. Schaeffer, III, *Science* **1972**, *176*, 1412. Copyright 1972, American Association for the Advancement of Science.)

[1] C. F. Bender, S. V. O'Neill, P. K. Pearson, and H. F. Schaeffer, III, *Science* **1972**, *176*, 1412.

(b) Three-dimensional energy
surfaces for $H_2 + F \rightleftharpoons$
$HF + H$
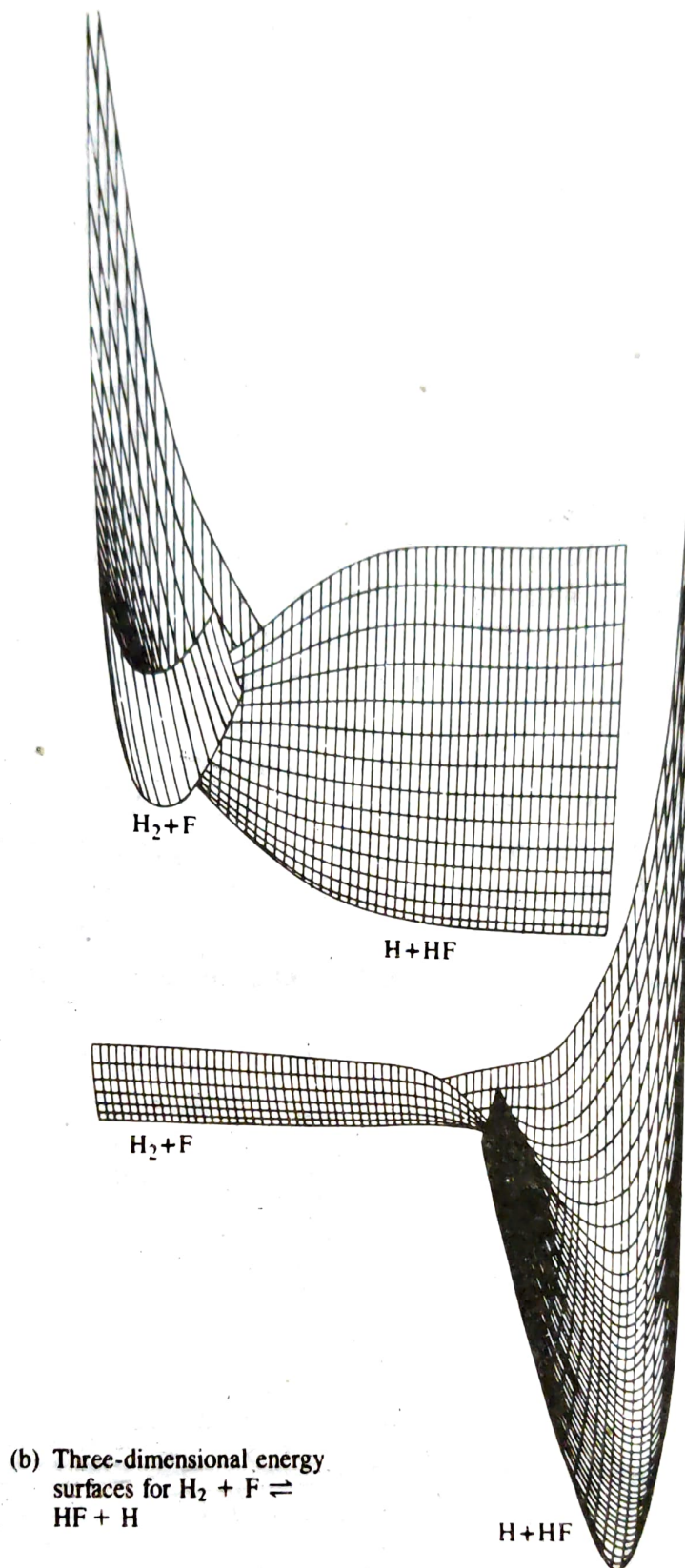
The intersection of the two parts of the potential surface in Figure 11.1*b* involves a saddle point (marked * in Figure 11.1*a*), which is an energy maximum as the reaction travels along the valleys of the plot (reaction coordinate), but a minimum along a path such as E–F. The surface around the point is saddle-shaped. Figure 11.1*c* is a two-dimensional plot of the system energy as it moves along the reaction coordinate, a so-called **reaction profile.**
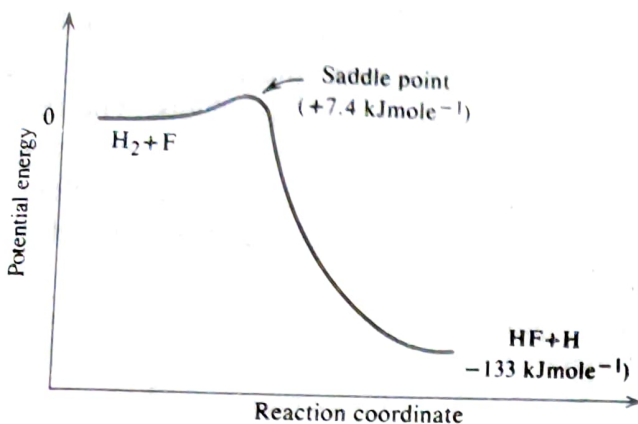
(c) Energy profile for $H_2 + F \rightleftharpoons H + HF$
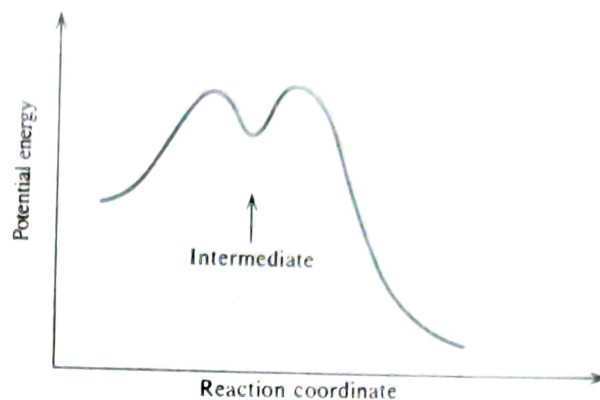
(d) Reaction profile showing an intermediate

Whether the $H_2 + F \rightarrow HF + H$ reaction proceeds forward or backward, it follows the reaction coordinate. Atomic positions simply reverse themselves as the reaction is reversed, like a film shown backwards. This is a statement of the **principle of microscopic reversibility.**

The principle of microscopic reversibility is extremely important in mechanistic studies, because it requires that *at equilibrium* both forward and reverse reactions proceed at equal rates along the reaction coordinate. Hence, the study of exchange reactions where leaving and entering groups X are the same is quite important, because the route of entry for the new ligand must be just the reverse of that for loss of the leaving ligand. *Insofar as some other entering ligand Y resembles the leaving one X*, the principle of microscopic reversibility places limitations on the possible mechanisms for replacement of X by Y; that is, we expect the mechanism to resemble that for replacement of X by X (exchange). This is true for each separate step of a multistep reaction. Instead of a saddle point, some potential surfaces (although not the HHF one) have a potential well or depression corresponding to a slightly stable configuration of reacting atoms, an **intermediate.** Slight stability means that the intermediate can persist for some small length of time. However, it eventually follows the reaction coordinate down into a valley. Figure 11.1d shows a reaction profile for a system with one intermediate. (Several successive intermediates are also possible in multistep reactions.)

The width of the low-energy valley is related to entropy requirements for the reaction. A steeply sloping and narrow energy valley is associated with very negative entropy of activation involving constriction of the reactant atomic motions. Conversely, a wide valley is associated with relative freedom in the motion and orientation of the reactants (more positive entropy of activation).

More complex reactions are hard to depict in plots of energy as a function of all the relative atomic positions. A nonlinear N-atom molecule has $(3N - 6)$ interatomic distances and angles that could be varied to change the energy [a linear molecule has $(3N - 5)$]. Thus, a plot of energy versus each coordinate would require a $(3N - 5)$-dimensional hyperspace [or $(3N - 4)$ for a linear system]. Also, calculating such a multi-dimensional energy surface is tremendously difficult and time-consuming—especially when our interest lies along the path of minimum energy from reactants to products.