Doug Balmer

Professor Dailey

Chem 502

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H_2CO vs. HCOH Isomers

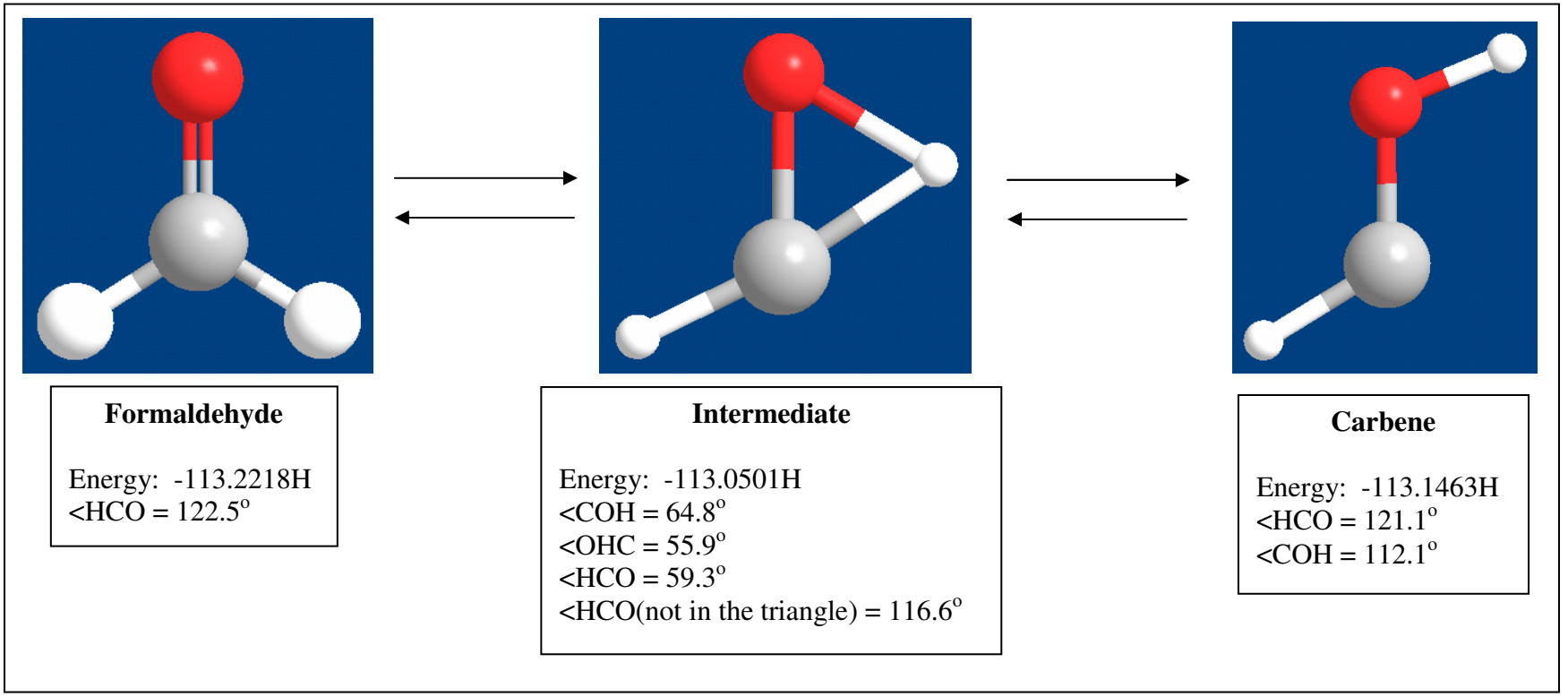

FIGURE 1 The equilibrium between formaldehyde and the HCOH carbene.

Figure 1, above, shows the equilibrium between formaldehyde and the HCOH carbene. As the formaldehyde changes to the carbene, the hydrogen swings up and starts to form a bridging bond with the oxygen. The hydrogen breaks its carbon bond to complete the process. The carbon and oxygen are both sp^2 hybridized in formaldehyde and the intermediate. The carbon is sp^2 hybridized in the HCOH carbene molecule. The hybridization of the oxygen depends on the resonance structures for the HCOH carbene (Fig.2). When there is a double bond between the carbon and oxygen to complete octets, the oxygen is sp^2 hybridized. When there is a single bond between the carbon and oxygen to reduce formal charges, the oxygen is sp^3 hybridized. Based on the C-O-H bond angle of 112.1^o shown in Figure 1, it appears the oxygen is between sp^2 and sp^3 hybridization.

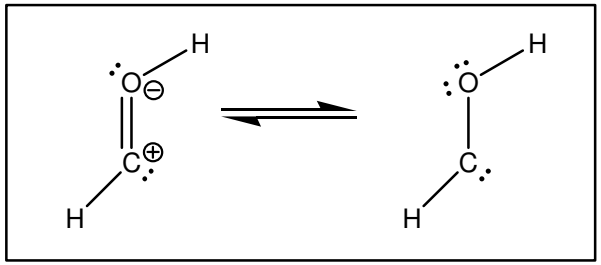

FIGURE 2 The resonance structures for the HCOH carbene.

Thermodynamics determines the stability of the H_2CO isomers and can be used to predict which isomer will dominate. The fact that formaldehyde is such a common chemical leads one to think that formaldehyde might be the more stable molecule. The GAMESS program was used to calculate the energy of each species shown in Figure 1. The program minimized the energy for the formaldehyde and the HCOH carbene, but found the saddle point for the intermediate. A saddle point is a local minimum on a plateau

of an energy surface diagram. Since the absolute energies are not that significant, the difference in energy between the different species had to be calculated. The difference in energy between the formaldehyde and the intermediate was 451kJ/mol (Eq. 1).

$$E_a = -113.0501H - -113.2218H = \mathbf{0.1717H}\ (627.51kcal/H) = \mathbf{107.7kcal/mol}\ (4.184kJ/1kcal) = \mathbf{451kJ/mol} \quad (1)$$

This energy corresponds to the activation energy for the conversion of formaldehyde to the HCOH carbene. The difference in energy between the HCOH carbene and the intermediate was 253kJ/mol (Eq. 2).

$$E_a \text{ reverse} = -113.0501H - -113.1463H = \mathbf{0.0962H}\ (627.51kcal/H) = \mathbf{60.4kcal/mol}\ (4.184kJ/1kcal) = \mathbf{253kJ/mol} \quad (2)$$

This corresponds to the activation energy for the conversion of the HCOH carbene to formaldehyde. The difference in energy between formaldehyde and the HCOH carbene was 198kJ/mol (Eq. 3).

$$\Delta H = -113.1463H - -113.2218 = \mathbf{0.0755H}\ (627.51kcal/H) = \mathbf{47.4kcal/mol}\ (4.184kJ/1kcal) = \mathbf{198kJ/mol} \quad (3)$$

This corresponds to the change in enthalpy, so the conversion between formaldehyde and the HCOH carbene is endothermic. Figure 3 shows the reaction coordinate for the conversion. Based on thermodynamics, formaldehyde is the more stable and favored species.

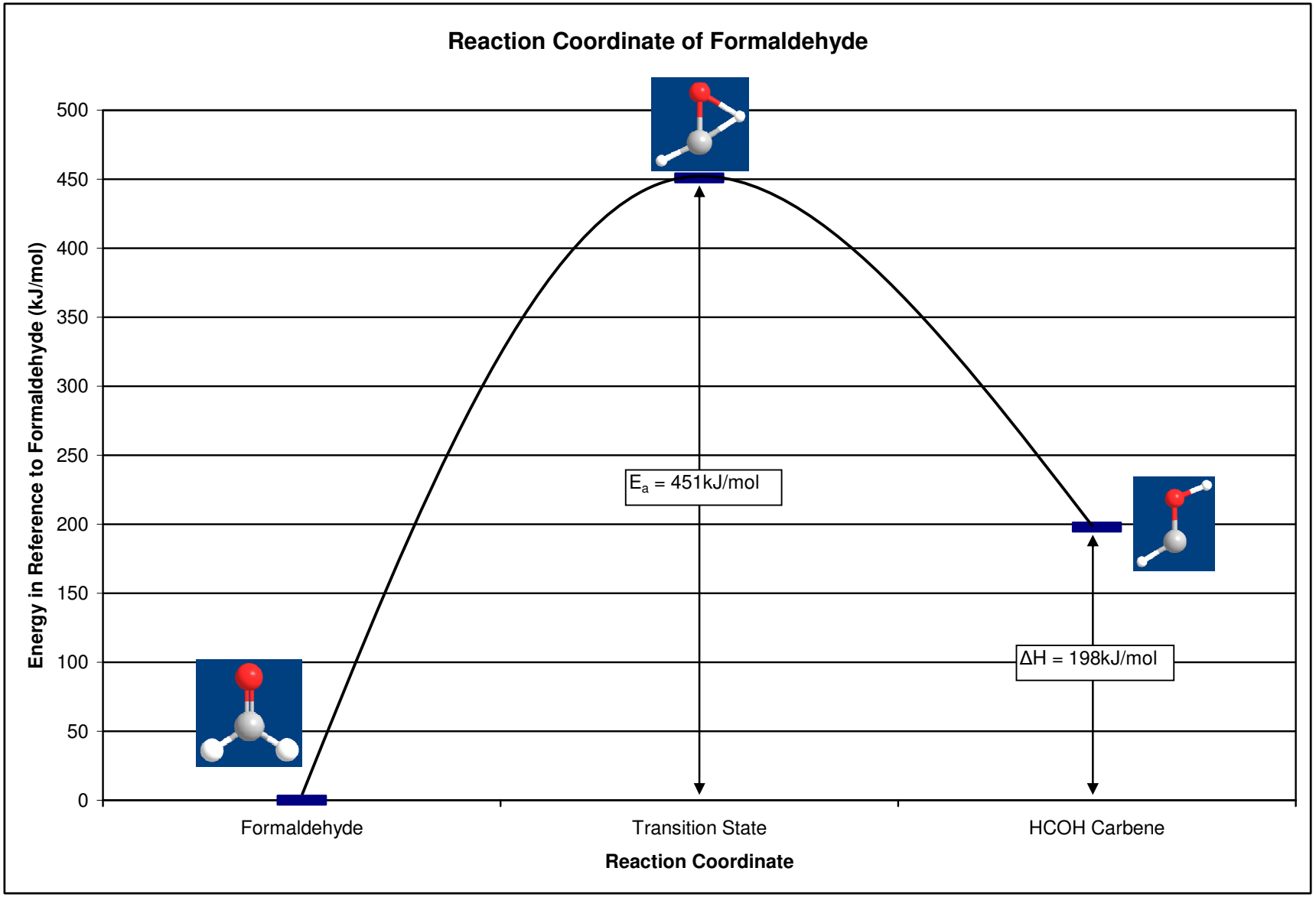

FIGURE 3 The reaction coordinate for the conversion of formaldehyde to the HCOH carbene.