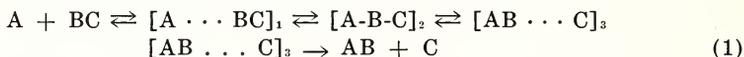


## The Investigation of Unstable Intermediates With the Aid of Infrared Radiation

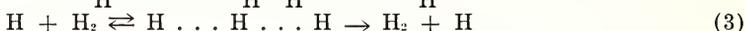
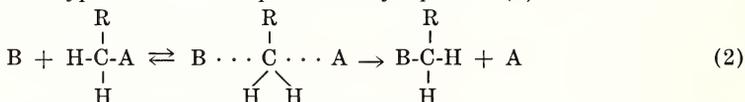
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A very large number of reactions are believed to proceed through the formation of unstable intermediates. Such a reaction may be indicated generally as



where  $[AB \cdots C]_1$  represents the transition state before the unstable intermediate,  $[A-B-C]_2$  is formed and  $[AB \cdots C]_3$  represents the transition state through which the unstable intermediate must pass in order to form the products.

One type of reaction represented by equation (1) is the  $S_N2$  reaction



or the hydrogen reaction

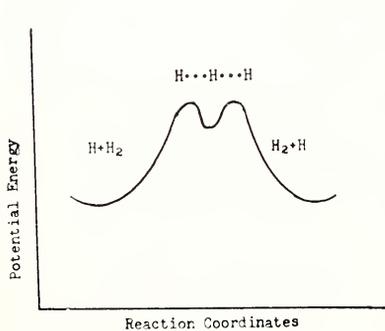


Figure 1

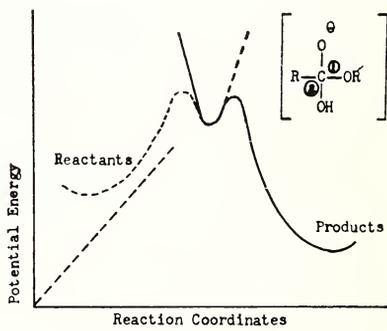
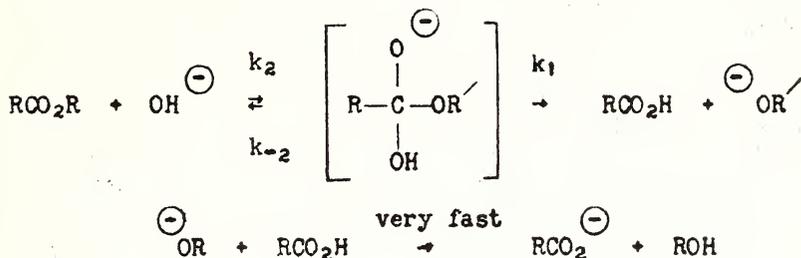


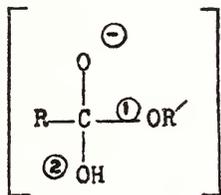
Figure 2

The potential energy barrier for the hydrogen reaction<sup>1</sup> is known to be approximately as indicated by figure 1. A valley of 2 to 2½ kcal in depth is believed to occur at the top of the potential energy barrier.<sup>1</sup> Since the three hydrogen atoms in the unstable intermediate are linear, only one reaction coordinate is necessary for describing the direction which the reaction follows. If energy could be selectively supplied to the unstable intermediate, the valley at the top of the potential energy barrier would be made more shallow and the overall rate of the reaction should remain unchanged. In other words the forward rate constant and the reverse rate constant would be increased proportionally by the same amount.

A different and more interesting example of equation (1) is the alkaline hydrolysis of esters which is believed to proceed by the following mechanism.<sup>2</sup>



This type of reaction differs from the  $\text{S}_{\text{N}}2$  and the hydrogen reactions in that two reaction coordinates must be used to describe the potential energy change during the formation and decomposition of the unstable intermediate.



These two reaction coordinates would be expected to have an angle of approximately  $109^\circ$  between them (see figure 2). Thus, it appears that if energy could be specifically introduced into bond ① or ②, the overall reaction could be speeded up or slowed down, respectively. If these two bonds absorb different frequencies in the infrared region, then monochromatic infrared radiation might serve as a means for energizing each bond separately. As much as 2 kcal per mole could be supplied to a specific bond which already has only a small energy barrier to overcome in order to break apart.

It should be pointed out that the ester mechanism was used only to present the basic idea and might well be a very poor system to study in this way.

The rate constant for the reaction represented by equation (4) can be expressed as

$$k = \left( \frac{k_1}{k_1 + k_{-2}} \right) k_2 \quad (5)$$

If  $k_1 \gg k_{-2}$ , then supplying energy to bond ② would have no apparent effect upon the overall reaction; however, supplying energy to bond ① would increase the overall rate of the reaction. If  $k_{-2} \gg k_1$ , then supplying energy to bonds ① or ② individually would respectively increase or decrease the rate of formation of the hydrolysis products.

In the third case where  $k_1 = k_{-2}$ , the reaction rate would be affected by the introduction of energy into either bond ① or bond ②. However, if equation (5) correctly represents the overall rate constant for the hydrolysis reaction, then the most ideal case for detecting whether selectively introduced energy affects the reaction rate is when  $k_{-2} \gg k_1$ .

In order to test the theory presented thus far, high intensity monochromatic, infrared radiation over a wide frequency range would have to be available. The reaction media would have to be chosen carefully to avoid the absorption of the desired radiation by the reactants or products. It is also possible that the specific bond could be deactivated by reemission or collision before bond rupture could occur.<sup>3</sup>

Even though the experimental difficulties for the investigation of the energetics of unstable intermediates by the use of infrared radiation appear to be enormous, it is very interesting that such an investigation is theoretically possible and may indeed become a reality in the very near future.

#### References

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