Chemistry: Bulgarian Journal of Science Education *Volume 25 Number 3, 2016* *Природните науки в образованието*

DETERMINATION OF ACTIVATION ENERGY IN NON-ISOTHERMAL CHEMICAL KINETICS

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Abstract. An alternative on the determination of activation energy in non-isothermal chemical kinetics is described.

Keywords: bromine, activation energy, chemical kinetics

A study on the determination of the activation energy of the oxidation of formic acid by bromine by non-isothermal method has been conducted (Hodgson et al., 1998). The reaction is believed to take place by the following mechanism (Brusa & Colussi, 1980):

$$HCOOH_{(aq)} + Br_{2(aq)} \rightarrow CO_{2(g)} + 2H^{+}_{(aq)} + 2Br^{-}_{(aq)} \quad (1)$$

$$HCOOH_{(aq)} \underset{k_{-1}}{\overset{k_1}{\Leftrightarrow}} H^{+}_{(aq)} + HCOO^{-}_{(aq))} \quad \text{rapid equilibrium} \quad (2)$$

$$HCOO^{-}_{(aq)} + Br_{2(aq)} \xrightarrow{k_2} CO_{2(g)} + H^{+}_{(aq)} + 2Br^{-}_{(aq)} \quad \text{slow} \quad (3)$$

By the rate-determining-step approximation, it has the rate law:

$$-d[Br_2]/dt = -d[HCOOH]/dt = \frac{k_1k_2[HCOOH][Br_2]}{k_{-1}[H^+]} \quad (4)$$

Since the rate of the reaction is dependent on hydrogen ion concentration, the addition of excess $HClO_4$ (strong acid) could simplify the rate law:

$$-d[HCOOH]/dt = k^*[Br_2] \quad (5)$$

where

$$k^* = \frac{k_1k_2[HCOOH]}{k_{-1}[H^+]} \quad (6)$$

The reaction is pseudo first-order with respect to $[Br_2]$. The activation energy of the reaction is then determined non-isothermally using the calculated value of k^*.

The addition of $HClO_4$ will not give the precise value of the activation energy since $HClO_4$ is a strong acid. Thus, the produced H^+ will shift the equilibrium (step 1) to the left side and dominates the reaction. Therefore, only a small amount of *HCOOH* is dissociated. Because the reaction is inversely first order to $[H^+]$, the calculated value of k^* will be smaller. This value does not represent the activation energy of the reaction.

Actually, the reaction can be performed only using *HCOOH*. Under the law of equilibrium, $[H^+]$ can be expressed in the concentration of *HCOOH* with the relation:

$$[H^+] = \sqrt{K_a[HCOOH]} \tag{7}$$

or

$$[H^+] = K_a^{1/2}[HCOOH]^{1/2} \tag{8}$$

If inserted into Eq. (4), this gives

$$-d[HCOOH]/dt = (k_1k_2/k_{-1}K_a^{1/2})[HCOOH]^{1/2}[Br_2] \tag{9}$$

The reaction is still first-order with respect to $[Br_2]$ but half-order to $[HCOOH]$ (Levine, 2009).

The use of an excess of $[HCOOH]$ will also make the reaction pseudo first-order with respect to $[Br_2]$ but it gives different value of rate-constant k^{**}:

$$-d[HCOOH]/dt = k^{**}[Br_2] \tag{10}$$

where

$$k^{**} = (k_1k_2/k_{-1}K_a^{1/2})[HCOOH]^{1/2} \tag{11}$$

The calculated value of k^{**} will be higher than k^* and so as to the activation energy. Theoretically, this value is more reliable and represents the activation energy of the reaction.

The above problem will be more interesting if the rate law is approached with steady-state approximation. Under this method, the rate law is

$$-d[HCOOH]/dt = \frac{k_1k_2[HCOOH][Br_2]}{k_{-1}[H^+] + k_2[Br_2]} \tag{12}$$

$$-d[HCOOH]/dt = \frac{k_1[HCOOH][Br_2]}{k_{-1}/k_2[H^+] + [Br_2]} \tag{13}$$

Let us back to the reaction mechanism. Supposedly, the reaction between $HCOO^-$ and Br_2 (step 2) will shift the equilibrium position (step 1) to the right. However, the same amount of produced H^+ ions will turn it back to the initial position and thereby ensuring that step 1 remains close to equilibrium. The implication is that, (*k-1/k2*) [H^+] can be considered constant and Eq. (13) becomes

$$-d[HCOOH]/dt = \frac{k_1[HCOOH][Br_2]}{K + [Br_2]} \tag{14}$$

According to Eq. (14), the reaction is first-order to [HCOOH], but the order with respect to [Br_2] will be depend on its concentration. If [Br_2] is relatively lower than *K*, the Eq. (14) turns into

$$-d[HCOOH]/dt = \frac{k_1[HCOOH][Br_2]}{K} \tag{15}$$

The reaction is also first-order to [Br_2]. Eq. (4) is the example of this case.

If [Br_2] is relatively much higher than *K*, Eq. (14) becomes

$$-d[HCOOH]/dt = k_1[HCOOH] \tag{16}$$

The reaction is the first-order to [*HCOOH*] but zero-order to [Br_2].

The use of an excess of [*HCOOH*] will change (16) to

$$-d[HCOOH]/dt = k^{***} \tag{17}$$

A question arises. Which equation should be used to determine the activation energy, i.e., Eq. (9) or (17)? Once again back to the reaction mechanism.

Since step 2 is the rate-determining step, the reaction is first-order to both [$HCOO^-$] and [Br_2]. It has been discussed that step 1 is always close to equilibrium. It means that [$HCOO^-$] is constant. Thus, the rate of the reaction is predominantly controlled by [$HCOO^-$]. If all $HCOO^-$ are reacted, the reaction reaches maximum velocity. The more addition of [Br_2] will not accelerate the reaction. This case is resemble with enzymatic reaction, where the activation energy is determined from v_{max} (Maire et al., 1991).1) Indeed, Eq. (14) can be taken as the example of the rate law of a reaction that similar to enzymatic reaction (Espenson, 1995). Finally, it can be concluded that, the best equation for the determination of the activation energy of this reaction is Eq. (17).

NOTE

1. http://classes.uleth.ca/200301/chem27102/expt_01.PDF

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