Rate expression for unimolecular gas-phase reaction

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Abstract: The prime purpose of this article is to establish a rate equation for unimolecular gas-phase reaction. [Manjunath.R. **Rate expression for unimolecular gas-phase reaction.** *Nat Sci* 2012; 10(12):98-99]. (ISSN: 15450740). http://www.sciencepub.net/nature. 15

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A unimolecular reaction is the breaking of a molecule into fragments:

$$A \rightarrow \text{Fragments}$$

To achieve this, A must gain sufficient energy to surmount the energy barrier. Excess energy gets into a particular vibrational degree of freedom. This vibration then produces dissociation of the molecule into fragments.

Lindemann (1922) explained the occurrence of unimolecular reactions by his famous mechanism. The Lindemann mechanism can be formulated by the scheme:

$$A + A \leftrightarrow A^* + A$$

$$A^* \rightarrow \text{Fragments}$$

where A represents inactive and A* activated molecules.

The first step is the activation. A collides with another A molecule to produce an activated molecule. A* has an excess energy, while the remaining molecule is deficient in energy. The activated molecule may be deactivated by collision or it may decompose into fragments.

The equilibrium constant for formation of active molecules, K* is:

$$K^* = n^* n / n^2 = n^* / n$$

We may resort to thermodynamics and write for K*

$$e^{-\Delta H^*/RT} e^{\Delta S^*/R} = n^* / n$$

where,

ΔH^* is the standard enthalpy of activation (The standard enthalpy of activation is approximately equal to the activation energy)

ΔS^* is the standard entropy of activation

Replacing ΔH^* by E_a we get

$$n^* = n\, e^{-Ea/RT} e^{\Delta S^*/R}$$

(E_a represents energy of activation)

But, fraction of molecules activated is given by the expression

n^*/n_0 = number of moles activated / total number of moles = $e^{-Ea/RT}$

and so we find that

$$n_0 = n\, e^{\Delta S^*/R}$$

Degree of unimolecular decomposition is the fraction of a mole of the reactant that underwent decomposition reaction. It is represented by α.

$\alpha = n_r / n_0$ = number of moles underwent decomposition reaction / total number of moles

Using the above equation we can arrive at

$$n_r = \alpha\, n\, e^{\Delta S^*/R}$$

According to transition state theory, the rate of unimolecular gas- phase reaction, is given by the expression,

Rate = (frequency of decomposition) × number of activated moles underwent decomposition reaction.

$$\text{Rate} = \nu^{\ddagger} n_r$$

But

$$\nu^{\ddagger} = (k_B T / h)$$

and, consequently,

$$\text{Rate} = (k_B T / h)\, n_r$$

Or, alternatively,

$$\text{Rate} = (k_B T / h)\, \alpha\, n\, e^{\Delta S^*/R}$$

(k_B is the Boltzmann constant and h is the Planck constant)

Further, since $n = P V / Z R T$ (Z represents compressibility factor), we can transform above equation to:

$$\text{Rate} = (P\ V / Z\ N\ h)\ \alpha\ e^{\Delta S^*/R}$$

"We have thus established the rate expression for unimolecular gas- phase reaction".

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