THE ACTIVATION ENERGY OF THE REACTION $H_2 + F \rightarrow H + HF$

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ABSTRACT: The London-Eyring-Polanyi-Sato (LEPS) and the modified London-Eyring-Polanyi-Sato (MLEPS) methods are used to calculate the activation energy of the reaction $H_2 + F \rightarrow H + HF$. It is found that the energy of activation calculated by MLEPS method is in much better agreement with the experimental result than by LEPS method.

INTRODUCTION

Extensive experimental results on the reaction $H_2 + F \rightarrow HF + H$ are not available because the reaction is so exothermic that it is difficult to control. Nevertheless Fettis and Knox (1964) have reported the energy of activation for the reaction to be 1.7 Kcal/mole, while Wilkins (1971) has reported the value to be 1.6 Kcal/mole. In the present work we apply both the London-Eyring-Polyanyi-Sato (LEPS) method and modified London - Eyring - Polanyi-Santo (MELPS) method to calculate the energy of activation of this reaction. The results obtained by the present calculation are compared with currently available data in the literature, as the relative merits of these two methods is discussed.

THEORY AND CALCULATIONS

The variation with interatomic distances of the potential energy E of a collinear three atom system XYZ can be readily calculated by the London equation (Glasstone, et al., 1941), $E = A + B + C - \{ \tfrac{1}{2} [(\alpha - \beta)^2 + (\beta - \gamma)^2 + (\gamma - \alpha)^2] \}^{1/2}$ (1) where A,B, C are the coulombic interactions of the pair of electrons on the atoms X and Y, Y and Z and Z and X, respectively, are α, β and γ are the corresponding exchange energies. The binding energy E_A of a diatomic molecule XY is dependent on the distance r between atoms, with reference to the energy of the separated atoms as zero; it is (Morse, 1929) $E_A = A + \alpha = D_A [\exp(-2_{A\rho_A}) - 2\exp(-2_{A\rho_A})]$ (2) where $\rho_A = r - r_{eA}$, D_A is the heat of dissociation of the molecule plus the zero point energy, r_{eA} is the equilibrium interatomic distance of the normal molecule and a_A is the Morse constant of the molecule. Eyring and Polanyi (Glasstone et al., 1941) suggested that the coulombic energies (A,B, and C) are a constant fraction (q) of the total binding energies, E, of the diatomic pair molecules XY, YZ and ZX. The q value usually ranges from 10 to 20%. Many activation energy calculations have been carried out by using this idea known as the London-Eyring-Polanyi (LEP) method. Sato (1955) modified the LEP method by introducing an anit-Morse function of the diatomic molecule XY.

$E_A{}^* = A - \alpha = D_A [\exp(-2a_{A\rho_A}) + 2\exp(-a_{A\rho_A})]/2$ (3)

so that coulombic energy or exchange energy is no longer a constant fraction of the total binding energy but can be well defined with the help of equations (2) and (3) as a function of interatomic distance, r, as $A = D_A[\tfrac{3}{4} \exp(-2_{A\rho_A}) - \tfrac{1}{2} \exp(-a_{A\rho_A})]$ (4)

$\alpha = D_A[\tfrac{1}{4} \exp(-2a_{A\rho_A}) - 3/2 \exp(-a_{A\rho_A})]$ (5)

This constitutes the London-Eyring-Polanyi-Sato (LEPS) method. Sato (1955) also offered an alternative method known as modified London-Eyring - Polanyi - Sato (MLEPS) method where A and α are calculated from the following equations:

$$E_A = \frac{A + \alpha}{1 + Z_A} = D_A \; [\exp \; (-2_{A\rho_A}) - 2 \exp \; (a_{A\rho_A})] \qquad (6)$$

$$E_A{}^* = \frac{A - \alpha}{1 - Z_A} = D_A \; [\exp \; (-2a_{A\rho_A}) + 2 \exp \; (-a_{A\rho_A})]/2 \qquad (7)$$

where Z_A is the overlap energy of the molecule XY. Solving equations (6) and (7) we have,

$$A = D_A \; [\, (3 + Z_A) \; \exp \; (-2a_{A\rho_A}) - 2 \; (1 + 3Z_A) \; \exp \; (-a_{A\rho_A})]/4 \qquad (8)$$

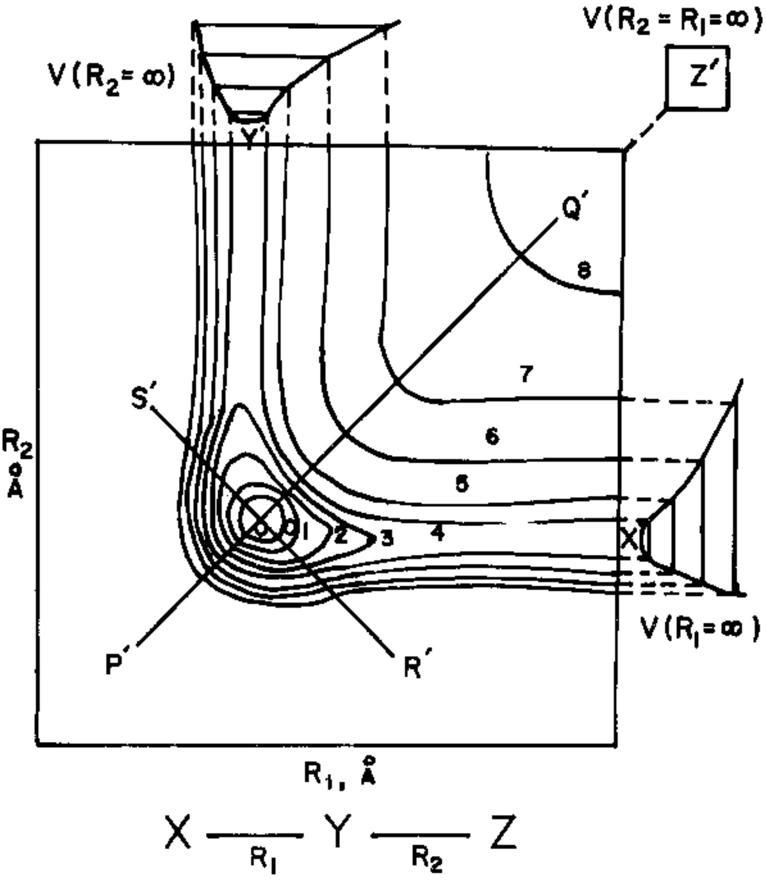

Fig. I. Potential Energy Surface of a Linear Triatomic Molecule XYZ.

$$= D_A \left[(1 + 3Z_A) \exp(-2a_A\rho_A) - 2(3 + Z_A) \exp(-a_A\rho_A) \right]/4 \qquad (9)$$

Similar expressions can also be obtained easily for B, β and C, γ in both LEPS and MLEPS methods.

To calculate the classical energy of activation of a reaction, the above expressions are first used to obtain the potential energy surface for XYZ a collinear three atom system. Then the stretching and bending force constants are calculated from the potential energy surface. There are four extrema in the potential energy surface of a linear triatomic molecule XYZ (see Fig. 1) they are 0', X', Y', and Z'. A Taylor series expansion can be made in each extremum of the potential energy surface. Near Z' the linear, quadratic and also all the higher terms in the Taylor series expansion are zero. Near the region Y' and X' only the quadratic terms of the Taylor series exist, which are the Force constants of the diatomic molecule XY and YZ respectively.

About the region O' three quadratic terms exist, they are

$$f_{11} = \frac{\partial^2 V}{\partial R^2_1},\ f_{22} = \frac{\partial^2 V}{\partial R^2_2} \text{ and } f_{12} = \frac{\partial^2 V}{\partial R_1 \partial R_2} \qquad (10$$

At a small departure from O', the potential energy can be discribed by the quadratic form,

$$V - V_O = (f_{11} r^2_1 + f_{22} r^2_2 + 2f_{12} r_1 r_2)/2 \qquad (11)$$

where

$$r_1 = R_1 - R_{10},\ r_2 = R_2 - R_{20}$$

Therefore the force constant for a line through O, parallel to the R_1 axis is,

$$f_{11} = 2\Delta/r_1{}^2 \qquad (12)$$

and that for the line through O, parallel to R_2 axis is,

$$f_{22} = 2\Delta V/r_2{}^2 \qquad (13)$$

The force constant f_{12} is calculated through O, for the line COD or EOF neither parallel to R_1 nor R_2. The value of the interaction force constant f_{12} can then be found from the equation,

$$f_{12} = [f_C (1+C^2) - f_{11} - C^2 f_{22}]$$

where,

$$f_C = f_{11} + C^2 f_{22} + 2Cf_{12} \qquad (14)$$

and

$$C = \frac{dR_2}{dR_1}$$

The potential energy function can be well expressed in terms of three co-ordinates R_1, R_2 and R_3. The bending angle Θ is related to the coordinates as

$$R^2_3 = R^2_1 + R^2_2 - 2R_2R_2 \operatorname{Cos} \Theta \qquad (15)$$

The angular force constant f_Θ is defiined by,

$$f = \frac{\partial^2 V}{\partial \Theta^2} = \frac{\partial}{\partial \Theta}\left(\frac{\partial V}{\partial \Theta}\right)$$
$$= \frac{\partial}{\partial \Theta}\left(\frac{\partial V}{\partial R_3} \bullet \frac{\partial R_3}{\partial \Theta}\right)$$
$$= \frac{\partial V}{\partial R_3}\left(\frac{\partial^2 R_3}{\partial \Theta^2}\right) + \left(\frac{\partial R_3}{\partial \Theta}\right)^2 \left(\frac{\partial^2 V}{\partial R^2_3}\right) \qquad (16)$$

$$f = -\frac{R_1 R_2}{R_3}\left(\frac{\partial V}{\partial R_3}\right)_{R_1, R_2} \qquad (17)$$

where the values of $\frac{\partial R_3}{\partial \Theta}$ and $\frac{\partial^2 R_3}{\partial \Theta^2}$ are obtained from equation (15).

The explicit equations for vibration frequencies of linear triatomic molecule are (Glasstone, et. al., 1941):

$\lambda_i = 1301.9\ \nu_i{}^{1/2}$ cm^{-1}, where $i = s$, l, Θ and

$\nu_s\ \frac{1}{2}\,[L + (L^2 - 4M)^{1/2}]$

$$\nu_1 = \tfrac{1}{2}\,[L - (L^2 - 4M)^{1/2}]$$

$$\nu\Theta = f\Theta\,[\frac{1}{\substack{2 \\ R_1M_X}} + \frac{1}{\substack{2 \\ R_2M_Z}}$$

$$+ (\frac{1}{R_1} + \frac{1}{R_2})^2 \frac{1}{M_Y}]$$

$$L = \frac{f_{11}}{M_X} + \frac{f_{22}}{M_Z} + \frac{f_{11} + f_{22} + 2f_{12}}{M_Y}$$

$$M = \frac{(f_{11}f_{22} - f^2_{12})\,(M_X + M_Y + M_Z)}{M_X\,M_Y\,M_Z} \quad (18)$$

In the above equations, f is in units of 10^5dyne/cm, $f\Theta$ is in units of 10^{-11} ergs/radian^2, R is in Units of A°. M_X,M_Y and M_Z are the masses of atoms X, Y and Z respectively and are in gram-molar mass units. λ_S is the stretching frequency, $\lambda\Theta$ is the bending frequency and λ_1 is an imaginary number, included to consider the penetration of the energy barrier. After obtaining the classical energy of activation E_C, (see Table II) the activation energy of reaction E_O can be evaluated by the following equation

$$E_O = E_C + N\ (\Sigma\tfrac{1}{2}h\upsilon_\sharp - \Sigma\tfrac{1}{2}h\upsilon_i) \quad (19)$$

where $\upsilon_\sharp$ is the zero point frequency of the activated state. The zero point energy of the activated state, $E^O{}_\sharp$ is

$$E^O\sharp = \tfrac{1}{2}\ (2\lambda\theta + \lambda_S) \quad (20)$$

because $\lambda\theta$ is doubly degenerate. Finally,

$$E_O = E_C + E^O{}_\sharp - E^O{}_i \quad (21)$$

where $E^O{}_i$ is the zero point energy of the initial component or components. The present calculations have been carried out on an IBM 360-M40 computer and the results are shown in Table I-III.

TABLE 1. Constants used in Determining the Morse Equation

	^reA(A)	D^e(Kcal/mole)	a	z
H_2	.74	109.4	1.94	.16
HF	.92	140.5	2.23	.16

TABLE 2. Calculated parameters for the activater.

	LEPS	MLEPS
R_1(Å)	0.8565	0.7553
R_2(Å)	1.3074	1.6036
f_{11}(mdyne/Å)	1.7648	5.0831
f_{22}(mdyne/Å)	-0.4559	-0.0798
f_{22}(mdyne/Å)	1.7017	0.3866
$f\Theta/R_1R_2$	0.0538	0.0149
E^c(Kcal/mole)	27.13	1.03

TABLE 3. Comparison of Energies of Activation Calculated by Different Methods.

	Present Calculation		LEP method (when coulombic binding energy is taken as	Wilkins' Calculation	Expt. Value
	LEPS method	MLEPS method	10 & 3.5 respectively		
λ_a (cm^{-1})	3439.3	4283.4			
λ_O (cm^{-1})	720.8	411.0			
λ_1 (cm^{-1})	989.11	307.6i			
E_0 (kcal/mole)	27.91	2.13	5-15	1.6	1.7

DISCUSSION:

From Table III one can see that the activation energy of the $H_2 + F \rightarrow H + HF$ reaction obtained by MLEPS method is in much better agreement with the experimental result than by LEPS method. The MELPS method appears to provide a potential surface free of deep basins. However, the MELPS method still appears to be quite as empirical as the LEP method because the true square of the Heitler-London overlap intergral at the activated-state configuration is usually three times greater than the value required in the MLEPS method. Moreover, there can be no justification for using a constant square of the Heitler-London overlap integral for $H_2 + F$ (the value in fact changes with the change of H-H distance in the activated region). Nor can the use of the same square of the overlap integral value in different reactions be justified. Therefore, it is not unexpected that the MLEPS method is inferior to Wilkins' (1971) calculation of the activation energy for the $H_2 + F \rightarrow HF + H$ reaction. It seems that the MLEPS method may not be a good quantitative method but still is a useful qualitative method for calculating the activation energy of a reaction because it gives reasonable results and does not involve any complicated computations.

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