

THEORETICAL CALCULATION OF ACTIVATION ENERGY FOR THE ADDITION OF HYDROGEN HALIDES TO ETHYLENE COMPOUNDS

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The activation energy for the addition of hydrogen halides to ethylene was calculated theoretically by the well-known semi-empirical method of Eyring. The calculations were further carried to the addition reaction of higher homologs of ethylene. Direct experimental data on the activation energy of these reactions are not available. In those cases where activation energy could be estimated from the reversed reaction, calculated values are in fair agreement with the experimental ones. The variation of Coulomb and exchange energy shows that the best fit is obtained by taking the Coulomb energy as 14 per cent and exchange energy as 86 per cent of the total as previously taken by Eyring.

INTRODUCTION

The C-C unsaturated bond of ethylene is very reactive in the sense that it undergoes addition reaction with halogens and hydrogen halides. The degree of readiness with which the reaction takes place is, however, different for different halogens and hydrogen halides. In fact the addition of hydrogen iodide proceeds readily even at room temperature although the addition of other halides takes place either at a higher temperature or in presence of a catalyst. The object of the present investigation was to make a theoretical calculation of activation energies for the addition of three hydrogen halides to some ethylenic compounds and find a basis for the difference in the behaviour of three hydrogen halides. It may be mentioned that such theoretical calculations had already been made by Sherman *et al.* (1936) as also by the Chinese workers Sun and Liu (1936) for the addition of halogens to ethylene.

THEORY

The method of calculation of activation energy for bimolecular chemical reactions is due to Eyring (1931). As the method has not been used very often, particularly during recent years, it is advisable to review the method briefly.

In this method all the valence electrons in a molecule are not treated alike. Instead one assumes that only certain electrons in a bond are changed during activation process. The other electrons are regarded as so firmly paired that they need not be considered in the calculation. That is the reaction



is regarded as a four electron system (the two electrons contributed by HCl and the two electrons which form the C-C π -bond in ethylene). Eyring (1931) supposed that the energy of interaction E of a system of two atoms might be divided into two parts

$$E = A + \alpha$$

where A is the Coulomb energy and α is the exchange energy, both of which depend upon the distances between the two atoms. The value of E for different values of the internuclear distance, r , may be obtained from the Morse equation for a diatomic molecule,

$$E = A + \alpha = D \{ \exp [-2a(r-r_0)] - 2 \exp [-a(r-r_0)] \}$$

where D is the sum of the dissociation energy and zero-point energy of the molecule and r_0 is the equilibrium bond distance; a is equal to $(2\pi^2/hc)^{\frac{1}{2}} \nu(\mu/D)^{\frac{1}{2}}$ and μ is the reduced mass of the molecule. For most diatomic molecules the values of D , r_0 , ν and μ are accurately known from spectra of diatomic molecules (Herzberg 1950). The total energy of interaction is then apportioned between the Coulomb and exchange energies. Eyring found that if Coulomb energy is taken as 14 per cent of total energy then best fit is obtained with experimental results for many reactions. The method, therefore, is a semi-empirical one in which Coulomb and exchange energies are not calculated theoretically but are estimated from spectroscopic data.

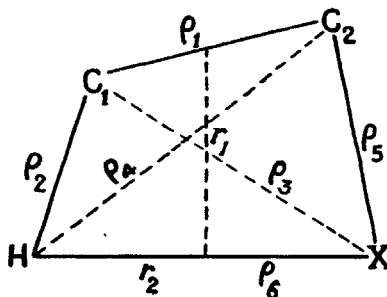


Fig. 1. Geometry of transition state for H-X addition to C=C bonds.

Assuming the H-X bond approaches the C-C bond (Fig. 1) asymmetrically in a plane, the angle between the H-X line and the perpendicular bisector of the C-C line was determined by considering that all the distances involved

were in the final position when the H-X addition has actually taken place. In the beginning of the reaction, C-X and C-H distances are large and the H-X distance has the normal equilibrium value. As the reaction proceeds, the former two distances decrease and the latter one increases.

Now the four atoms C, C, H and X may be taken in six different ways, two at a time, C₁-C₂, C₁-H, C₁-X, C₂-H, C₂-X, X-H. Each of these pairs may be regarded as a separate diatomic molecule with interatomic distance $\rho_1, \rho_2, \rho_3, \rho_4, \rho_5$ and ρ_6 and with interaction energies $A_1 + \alpha_1, A_2 + \alpha_2, B_1 + \beta_1, B_2 + \beta_2, C_1 + \gamma_1$, and $C_2 + \gamma_2$. It can be shown that the total energy of such a system of four atoms, relative to the energy of the system in which the four atoms are infinitely far apart, is

$$E = A_1 + A_2 + B_1 + B_2 + C_1 + C_2 + \sqrt{\frac{1}{2}[(\alpha_1 + \alpha_2 - \beta_1 - \beta_2)^2 + (\beta_1 + \beta_2 - \gamma_1 - \gamma_2)^2 + (\gamma_1 + \gamma_2 - \alpha_1 - \alpha_2)^2]}.$$

The values for the Coulomb and exchange energies for any chosen interatomic distance $\rho_1, \rho_2, \rho_3, \rho_4, \rho_5$ and ρ_6 may be found from the Morse equation and inserted into the above equation to obtain the total energy of each configuration. Extensive potential energy surface may now be mapped out point by point from which the path of least gradient will give the path of reaction and the height of the hill above the valleys will give the activation energy.

The values of E calculated as above refers to the four atoms completely separated in space as zero energy. But we are interested in energy referred to the stable C = C and H-X compounds as zero (corresponding to the valley floors rather than to the high plateaus). Accordingly it is necessary to subtract these values of E from the total energy D required to break both the C-C and H-X bond to get the required potential energy. It may be observed that because of the assumed geometry of the transition state all distances ρ_1 to ρ_6 are not independent. If two independent variables are r_1 and r_2 , where r_1 is defined as the distance separating the C-C and H-X bond and r_2 as the distance separating H and X, all other distances can be related to these two distances. In making the contour map the corrected E is plotted against the values r_1 and r_2 (plotted as X and Y coordinates of a Cartesian coordinate system). Lines are then drawn at constant values of E which gives the two-dimensional projection of potential energy surface. The activation energy is then estimated from the lowest pass between the valleys.

RESULTS

The various constants used in the construction of Morse curve are summarized in Table I (Herzberg 1950).

The two-dimensional contour maps constructed for the addition of HCl, HBr and HI to ethylene are shown in Figs. 2-4.

TABLE I
Bond constants for Morse curve

Bond	r_0 (Å)	ν_0 (cm ⁻¹)	D (k-cal/mole)
C-C	1.46	—	61.0
C-H	1.12	2930	92.3
C-Cl	1.76	655	78.6
C-Br	1.91	557	63.3
C-I	2.10	497	56.5
H-Cl	1.28	2840	101.5
H-Br	1.42	2603	82.1
H-I	1.62	2233	69.0

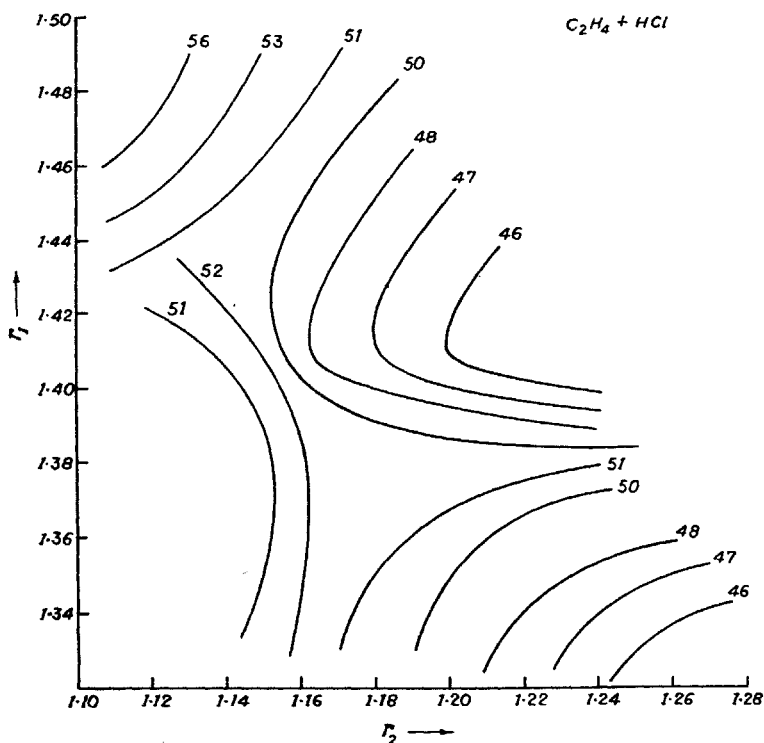


FIG. 2. Potential energy surface for HCl addition to ethylene.

The activation energies estimated from these maps are summarized in Table II.

DISCUSSION

The calculated result depends strongly on the values of the constants used in the construction of Morse equation. As these constants have been

used from spectra of diatomic molecules, they are known very accurately, at least they are more exact than the experimental accuracy of activation energy measurements. On the basis of activation energy calculation it is expected that HI would add more readily to ethylene than HCl or HBr.

A direct comparison of theoretical and experimental activation energy is not possible because the data reported in literature refers to the activation

TABLE II
Calculated activation energy for addition of hydrogen halides to ethylene as compared with the observed values for the reversed reaction

Reaction	E for reversed reaction Expt.	Activation energy (k-cal/mol)
$C_2H_4 + HCl$	60.8 ^a	50.5
$C_2H_4 + HBr$	53.9 ^b	40.0
$C_2H_4 + HI$	52.8 ^c	36.0

a. Barton and Howlett (1949).

b. Green, Harden, Maccoll and Thomas (1953).

c. Yang and Conway (1965).

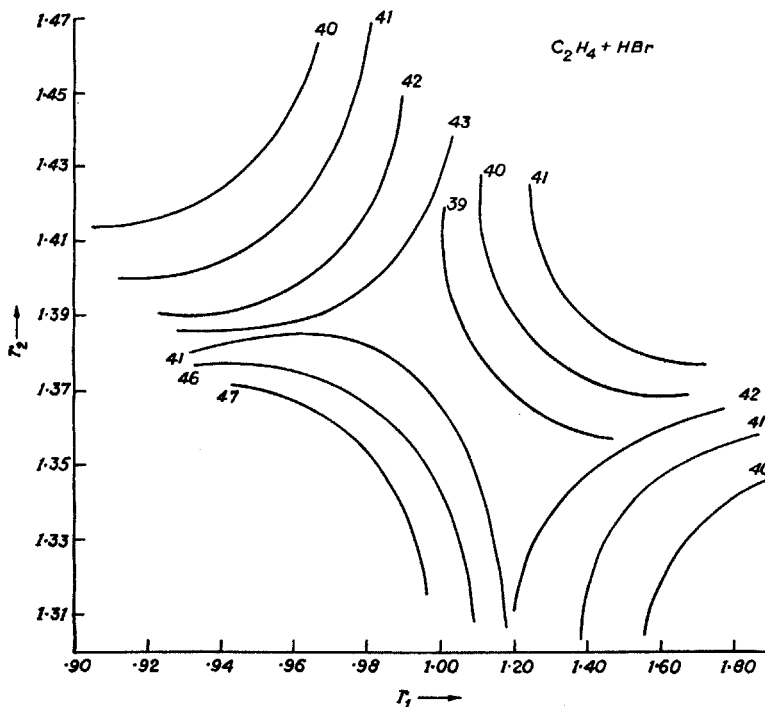


FIG. 3. Potential energy surface for HBr addition to ethylene.

energy of the reversed reaction, i.e. dehydrohalogenation reaction. If the heat of reaction is known, then the sum of the activation energy of hydrogen halide addition to ethylene and heat of reaction will give the activation energy for dehydrohalogenation reaction.

The theoretical value of activation energy for HCl addition to ethylene is 50.5 and the heat of reaction is 15 ± 1 k-cal. Thus the theoretical activation energy for dehydrohalogenation reaction of ethyl chloride which is 65.5 k-cals compares favourably with the experimental value of 60.8.

There is one arbitrary assumption in the whole procedure, and that is the assumption that the Coulomb term is 14 per cent of the total interaction energy. In order to test how the calculation is affected by letting the Coulomb term vary, the activation energy for HCl addition to ethylene was calculated using Coulomb energy as 10 per cent, 14 per cent and 20 per cent of the total interaction energy. Calculated activation energies are tabulated below:

Coulomb energy ..	10%	14%	20%
Activation energy ..	66.0	50.5	27.0

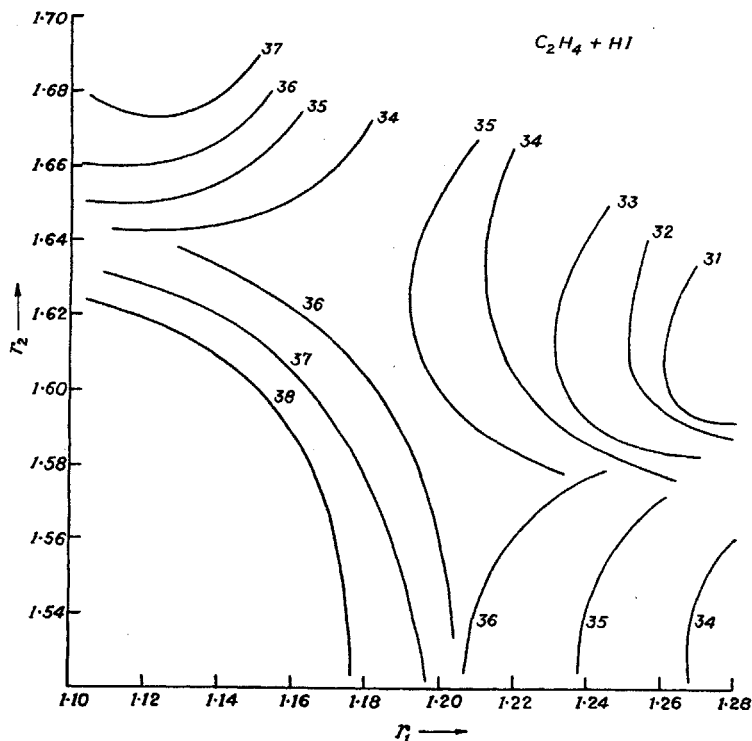


Fig. 4. Potential energy surface for HI addition to ethylene.

It is evident that best agreement with experiment is obtained when the Coulomb term is taken as 14 per cent of the total interaction energy.

It should be admitted that absolute calculation of activation energies is not possible with the approximation of electron pairing, because the chemical transformation is, by its very nature, a transformation from one bond type to another and activation hill is just the zone where affinities are being changed and there is no natural system of partnership. If, however, our interest lies in the relative energies, as is usually the case in predicting chemical reactivity, then the calculation may not be affected too much by the simplifying assumptions.

In the calculation of activation energy for other ethylenic compounds the Morse curve for C-C bond only had different constants as tabulated below. Rest of the calculations were the same as before. The calculated activation energies are given in Table III.

Bond constants for Morse curve

C = C bond in compounds	$\nu_0(\text{cm}^{-1})$	D_0 (k-cal/mole)
$\text{CH}_3\text{CH} = \text{CH}_2$	1643	101.50
$\text{CH}_3\text{CH}_2\text{CH} = \text{CH}_2$	1647	101.88
$\text{CH}_3\text{CH} = \text{CHCH}_3$	1673	103.58

TABLE III

Calculated activation energy for addition of hydrogen halides to higher homologues of ethylene and the observed values for the reversed reaction

Compounds	HX	Activation energy	
		Calculated	Experimental (reversed reaction)
$\text{CH}_3\text{CH} = \text{CH}_2$	HCl	44	55.0 ^a
$\text{CH}_3\text{CH} = \text{CHCH}_3$	HCl	45	50.1 ^b
$\text{CH}_3\text{CH}_2\text{CH} = \text{CH}_2$	HCl	44.5	57.0 ^a
$\text{CH}_3\text{CH} = \text{CH}_2$	HBr	35.0	50.7 ^c
$\text{CH}_3\text{CH}_2\text{CH} = \text{CH}_2$	HBr	33.0	50.9 ^d
$\text{CH}_3\text{CH} = \text{CHCH}_3$	HBr	34.0	46.5 ^e
$\text{CH}_3\text{CH}_2\text{CH} = \text{CH}_2$	HI	27.5	
$\text{CH}_3\text{CH} = \text{CH}_2$	HI	25.0	
$\text{CH}_3\text{CH} = \text{CHCH}_3$	HI	26.0	

^a. Barton, Head and Williams (1951). ^b. Stone, M.Sc., Thesis (1958), University of London (Cf. Maccoll and Thomas 1957). ^c. Blades and Murphy (1952). ^d. Maccoll and Thomas (1957). ^e. Kale, M. N., Ph.D. Thesis (1957), University of London (Cf. Maccoll and Thomas 1955).

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