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Predictions of the Features of the Potential Energy Surfaces from the Diatomic Constants: A Series of Collinear Abstraction Reactions, H+HX (X=F, Cl, Br, I)

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A new method, to predict the feature of potential energy surface (PES) from the diatomic constants of reactants molecules, is presented. The PES is calculated by using our proposed semi-empirical method (MT method). Based on MT method, a graphical method is introduced to investigate the relations between the features of the PES and the diatomic constants. Using these relations as guideline, the features of the PES for a series of linear abstraction reactions, H+HX=HH+X with X=F, Cl, Br, and I, are deduced in a simple manner. The PES thus deduced are in good agreement with available experimental and theoretical information.

The knowledge of topological features of potential energy surfaces (PES), such as potential barrier height and location, reaction-path curvature, etc. is of fundamental importance for the theoretical understanding of chemical reaction processes. In recent years, there have been remarkable advances in quantum mechanical computations of PESs by ab initio methods. However, ab initio computations of this kind are complicated, and the results defy simple, intuitive interpretation. In spite of the capability of modern computers, such calculations require a great deal of computer time, and can be carried out only for rather simple systems. For these reasons, methods for semi-empirical estimation of PESs are of considerble value. The early ingenious semi-empirical method of Ering and Polanyi,[1)] as later modified by Sato,[2)] is widely known as the LEPS method. In the LEPS method, which starts with a quantum mechanical energy expression based on valence bond theory (London's expression),[3)] a PES is constructed from diatomic Morse and anti-Morse potential functions, each of which involves three diatomic constants, i.e., the dissociation energy D, range parameter α, and equilibrium internuclear distance R_e. Besides of its simplicity one of the advantages of the LEPS method is that the PES of a three- or four-atomic system can be immediately correlated with the diatomic constants mentioned above. However, this advantage results from the neglect of all overlap and multiple-exchange terms in London's expression. In the past thirty years, other semi-empirical methods have been put forward by various authors: among them, the PK,[4)] DIM,[5)] and GDIM[6—8)] methods are widely known.

In previous papers,[9,10)] the present author proposed a new semi-empirical method, herein referred to as the MT method. In the MT method, all overlap and multiple-exchange terms, which were neglected in the London's energy expression, are evaluated; moreover, the connection between the computed PES and the diatomic constants is easily found. In other papers,[11,12)] the author, on the basis of this conection, discussed how the PES of a system consisting of three or four hydrogen atoms changes when the hydrogen atoms are replaced by heteroatoms X. In the present paper, which is a sequel of these papers, a graphical method is employed to examine the connection between the PES of the linear H–H–H system and of the linear H–H–H system. The Morse function for the diatomic molecule H–X has D, α, and R_e values which are different from those of H–H. The effects of varying these constants on the features of the PES is closely examined. In addition, by using these results as a guideline, the special cases when X is a halogen atom are considered; the purpose is to deduce the features of the PES for a series of linear abstraction reactions, H+HX=HH+X with X=F, Cl, Br, and I, in a simple manner. Finally, the PES thus deduced are examined by comparing them with available experimental and theoretical information, and the utility of the method is demonstrated.

Theoretical

Remarks on the MT Method: In 1964 Porter and Karplus (PK)[4)] proposed a new analytic semi-empirical method for calculating the ground state PES of the H_3 system. They tried to improve the LEPS method by including overlap and multiple-exchange terms in the energy expression and showed a practical way of computing these terms. The present author's MT method differs from the PK method in the evaluation of the multiple-exchange terms; furthermore, the MT method has been generalized to n-electron, n-atom systems in the following respects.

Based on the nonionic valence bond theory,[13)] the potential energy E of an n-electron, n-atom system is given by roots of the secular equation:

$$|\boldsymbol{H} - \boldsymbol{M}E| = 0 \tag{1}$$

where $\boldsymbol{H}$ and $\boldsymbol{M}$ are a Hamiltonian matrix and a function of the overlap integrals, respectively. The matrix $\boldsymbol{H}$ can be expressed in terms of multiple-exchange integrals (Λ_p) which are defined as

$$\Lambda_p = \langle\Omega|H|p\Omega\rangle, \tag{2}$$

where Ω is Hartree product of the atomic orbitals, and $\boldsymbol{P}$ is the permutation operator of electrons.

The multiple-exchange integrals have been classified into three types; one is a transposition type Δ_p^1; another is a cycle type Δ_p^2; and the other is a mixed type Δ_p^3 of Δ_p^1 and Δ_p^2.[10] By using the Mulliken approximation,[14] we have shown that first two types Δ_p^1 and Δ_p^2 are reduced to diatomic exchange α_i, Coulomb Q_i, and overlap S_i integrals as follows:

$$\Delta_p^1 \simeq (\Pi S_i^2)[Q + \Sigma(\alpha_i/S_i^2 - Q_i)], \tag{3}$$

$$\Delta_p^2 \simeq (\Pi S_i)[Q + \Sigma(\alpha_i/S_i^2 - Q_i)/2] \tag{4}$$

where $Q = nE_H + \sum_{i=1}^{3n-6} Q_i$, E_H is the energy of an atom. Moreover, the last mixed type Δ_p^3 was proved to be expressed in terms of Δ_p^1 and the Δ_p^2 as

$$\Delta_p^3 = (\Pi S_i^2)(\Pi S_j)[\Delta_p^1/(\Pi S_i^2) + \Sigma(\Delta_p^2/(\Pi S_j) - mQ] \tag{5}$$

where m was the number of the cycle.

As a result, all integrals included in Eq. 1 are reduced to "diatomic components" α_i, Q_i, and S_i. Since the "diatomic components" are a properties of the reactant molecule, the method can be applied to many reaction systems by exchanging the value of "diatomic components". This is the most important characteristic of the MT method, because in other semi-empirical methods the multiple-exchange integrals have been evaluated empirically in more complicated ways[4,15] specific to each system, or simply neglected.[1-3]

The analytical expressions for the "diatomic components" α_i, Q_i, and S_i are well-known. The first two diatomic components, α_i and Q_i are expressed in terms of the Morse and anti-Morse functions as

$$\alpha_i = [(^1E_i - {^3E_i}) + S_i^2(^1E_i + {^3E_i})]/2, \tag{6}$$

$$Q_i = [(^1E_i + {^3E_i}) + S_i^2(^1E_1 - {^3E_i})]/2, \tag{7}$$

$$^1E_i(R_i) = D\{\exp[-2\alpha(R_i - R_e)] - 2\exp[-\alpha(R_i - R_e)]\}, \tag{8}$$

$$^3E_i(R_i) = \eta\{\exp[-2\beta(R_i - R_e)] + 2\exp[-\beta(R_i - R_e)]\}, \tag{9}$$

where ^1E and ^3E are the Morse and anti-Morse functions for the diatomic molecule in the singlet and triplet states, respectively; and η and β are adjustable parameters in ^3E_i, and they may calculated by ab initio methods. The analytical expression for the last "diatomic component" S_i is known to be[4]

$$S_i = (1 + R_i\zeta + R_i^2\zeta^2/3)\exp(-R_i\zeta) \tag{10}$$

where ζ is the orbital exponent of the atomic orbital, and its variation with the interatomic distance R_i can be approximately expressed as

$$\zeta = 1.0 + \kappa\exp(-\lambda R_i). \tag{11}$$

Whereas Porter and Karplus[4] determined the values of the parameters κ and λ in Eq. 11 by using the numerical result of Wang's variational calculation[16] of the hydrogen molecule, the present author proposes that these parameters be used as adjustable parameters as explained below.

It should be noted that the evaluations of potential energy surfaces by the MT method are reduced to calculations of "diatomic components" α_i, Q_i, and S_i, so that they are expressed in analytical functions as in Eqs. 6, 7, and 10. Therefore, potential energy E in Eq. 1 is expressed generally as a function of internuclear distances R as follows:

$$E = F(\chi_i, \tau; R) \tag{12}$$

where χ_i and τ are abbreviation for the diatomic constants of the i-th pair and for the adjustable parameters $(\eta, \beta, \kappa, \lambda)$, respectively. Equation 12 shows that the PES can be calculated by determining the diatomic constants χ_i of the reactant molecules and adjustable parameters τ.

Construction of the Standard and Reference PES: To see the effects of heteroatom substitution on a PES mentioned in introduction, we proceed as follows. The PES of the linear H–H–H system is computed by using MT method, and used a standard PES. In the computation, the H–H Morse and anti-Morse functions for the atomic pairs, H_a–H_b, H_b–H_c, and H_a–H_c, are used, where H_a and H_c stands for the end hydrogen atoms and H_b stands for the central one. For the H_2 Morse function, Eq. 8, the following values of the diatomic constants are used:

$$D = 0.1744 \text{ hartree}, \alpha = 1.05 \text{ bohr}^{-1}, R_e = 1.40 \text{ bohr}. \tag{13}$$

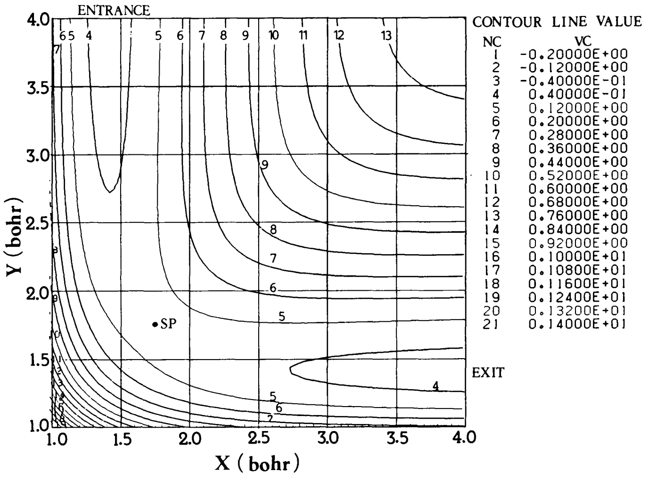
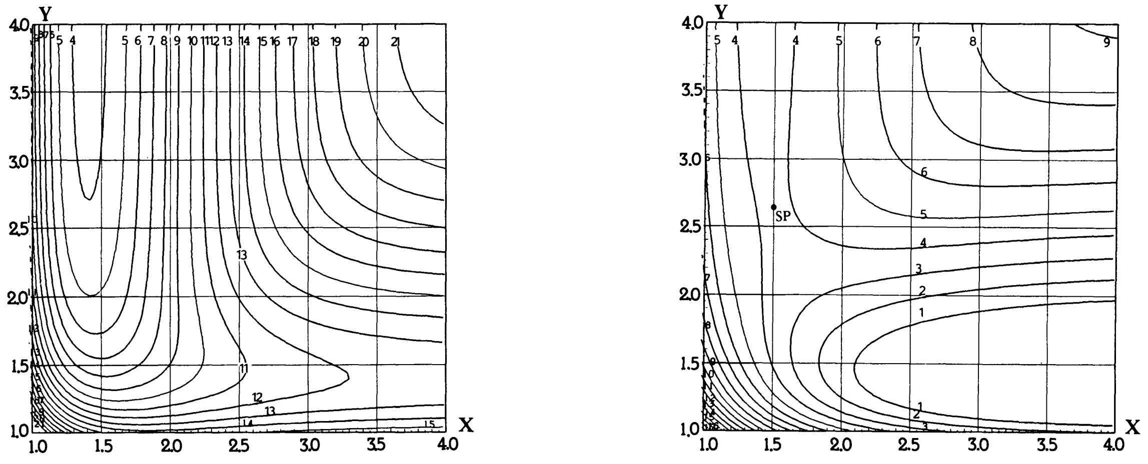
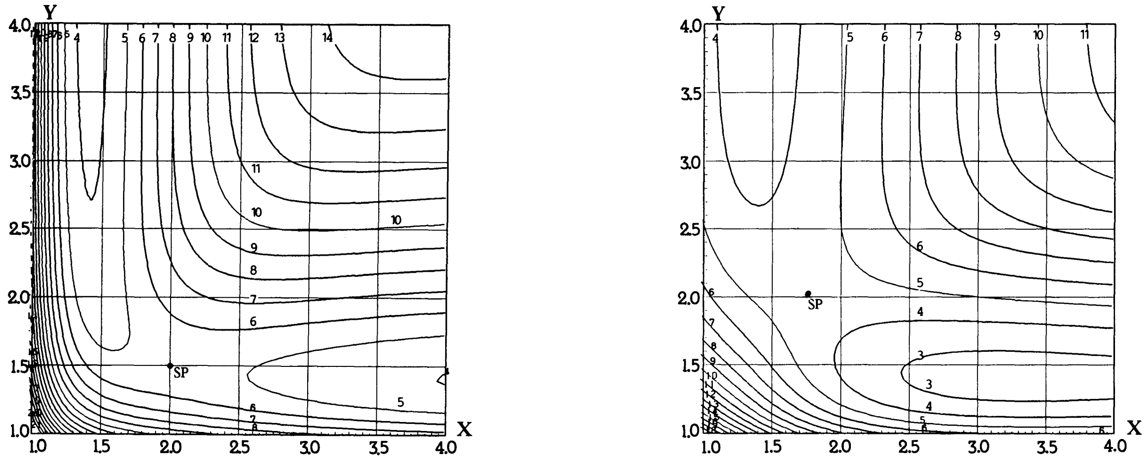


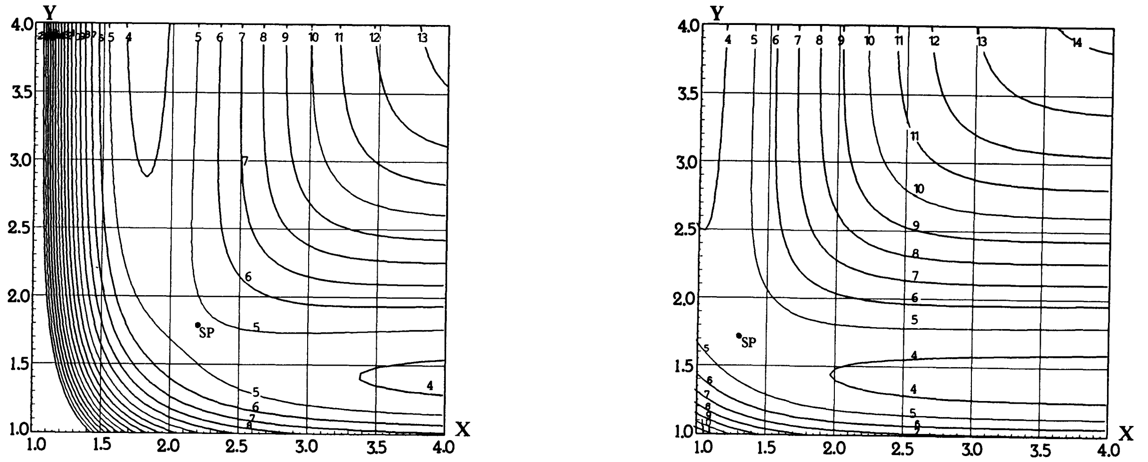
Fig. 1. The standard linear H_3 contour map. The contour intervals are 1/25 of the H_2 dissociation energy. The number and value of each contour line are denoted by NC and VC, respectively.



(a) D=0.35 (b) D=0.10



(c) $\alpha = 1.50$ (d) $\alpha = 0.60$



(e) Re = 1.80 (f) Re = 1.00

Fig. 2. The contour maps for the linear HHX system with different values of D, α, R_e (see text). The contour intervals are 1/25 of the H_2 dissociation energy. The X-axis and Y-axis show the internuclear distance of H–X and H–H, respectively.

For the H_2 anti-Morse function Eq. 9, the values,

$$\eta = 0.0729\,\text{hertree},\ \beta = 1.036\,\text{bohr}^{-1} \tag{14}$$

are employed. The numerical values in Eqs. 13 and 14 have been determined by the results of the precise ab initio calculation for the hydrogen molecule by Kolos and coworkers.[17] For the two adjustable parameters occurring in Eq. 11, the values

$$\kappa = 3.20,\ \text{and}\ \lambda = 1.202\,\text{bohr}^{-1} \tag{15}$$

are chosen to fit the computed H_3 PES at the saddle point and in its vicinity, to the result of Liu's precise ab initio calculation of the H_3 system.[18] All these parameters are given these standard values throughout the following.

The PES so obtained for H_3 is shown in Fig. 1, where the X- and Y-axes represent the H_b–H_c and H_a–H_b distances, respectively. This PES agrees fairly well with the Truhlar-Horowitz PES for linear H_3,[19] which is based on Siegbahn and Liu's precise ab initio calculations[18,20] of the H_3 system.

Now suppose that the end atom H_c is replaced by a heteroatomic X. The PES for this linear H–H–X system is calculated in the same way as the H–H–H PES, except that the H–H Morse functions for H_a–H_c and H_b–H_c in the H–H–H calculation are replaced by the H–X Morse functions, whose D, α, and R_e values are different from those in Eq. 13. To get an idea of how the PES changes by varying these diatomic constants in Eq. 13, six reference contour maps are computed by varying the three constants individually. The results are shown in Figs. 2(a)—(f), where the X- and Y-axes represents the H_b–X and H_a–H_b distances, respectively. The caption of Fig. 2(a), D=0.350 implies that the diatomic constants for H–X are taken to be the same as those for H–H given in Eq. 13, except that D=0.350 hartree is used; also it is assumed that the four parameters in Eqs. 14 and 15 remain unchanged. Captions of similar meaning are attached to Figs. 2(b)—(f). The use of these reference contour maps is described in the next section.

Results and Discussion

Diatomic Constants and the PES of the H–H–X System: Consider the cross section of the PES of the linear H–H–X system by a plane S which is perpendicular to the (X, Y)-plane and parallel to the X-axis. Obviously the cross section continuously approaches the potential curve of the diatomic molecule H–X as the distance between the plane S and the X-axis increases. Owing to this continuity, the features of the entrance valley of the H–H–X PES are immediately deduced from the features of the H–X potential curve.

Interesting points to be noticed as regards Figs. 2(a)—(d) are as follows. We observe in Figs. 2(a) and 2(c) that making D or α greater than the standard values (D=0.1744 or α=1.05) shifts the location of the saddle point to the exit valley side ("late barrier"), and makes the reaction-path curvature larger (a sharper bend of reaction path). Similarly, Figs. 2(b) and 2(d) indicates that making D or α smaller than the standard value shifts the saddle point to the entrance valley side ("early barrier"), and makes the reaction-path curvature smaller.

More quantitative information derived from similar calculations is shown in Tables 1—3 and Figs. 3—7. The trend found in Figs. 2(a) and 2(b) is more evident in Table 1, which indicates how the barrier height E_a, the saddle point location (X_a, Y_a), and the bond extensions ΔR_{HX} and ΔR_{HH} at the saddle point (BESP), change as D is varied. Here ΔR_{HX} and ΔR_{HH} are given by

$$\Delta R_{HX} = X_a - R_e,\ \Delta R_{HH} = Y_a - R_e,$$

Table 1. The Relations of Dissociation Energy D with Barrier Height E_a, Saddle Point Location (X_a, Y_a), BESP ΔR_{HX}, ΔR_{HH}, and Energy Defect ΔE

$D^{a)}$	$E_a^{b)}$	$(X_a, Y_a)^{c)}$	$\Delta R_{HX}^{c)}$	$\Delta R_{HH}^{c)}$	$\Delta E^{b)}$
0.250	47.25	(6.20, 1.40)	4.80	0.00	47.45
0.220	28.73	(4.20, 1.40)	2.80	0.00	28.61
0.200	17.77	(2.30, 1.50)	0.90	0.10	16.05
0.1744	9.80	(1.74, 1.74)	0.34	0.34	0.00
0.150	6.37	(1.55, 2.05)	0.15	0.65	−15.35
0.100	3.54	(1.50, 2.65)	0.10	1.25	−46.75

a) In units of hartree. b) In units of kcal mol^{-1}. c) In units of bohr.

Table 2. The Relations of Range Parameter α with Barrier Height E_a, Saddle Point Location (X_a, Y_a), and BESP ΔR_{HX}, ΔR_{HH}

$\alpha^{a)}$	$E_a^{b)}$	$(X_a, Y_a)^{c)}$	$\Delta R_{HX}^{c)}$	$\Delta R_{HH}^{c)}$
1.50	15.92	(2.00, 1.50)	0.60	0.10
1.20	11.24	(1.80, 1.60)	0.40	0.20
1.05	9.802	(1.74, 1.74)	0.34	0.34
0.80	9.00	(1.70, 1.94)	0.30	0.54
0.60	9.04	(1.74, 2.04)	0.34	6.40

a) In units of bohr^{-1}. b) In units of kcal mol^{-1}. c) In units of bohr.

Table 3. The Relations of Equilibrium Ditance R_e with Barrier Height E_a, Saddle Point Location (X_a, Y_a), and BESP ΔR_{HX}, ΔR_{HH}

$R_e^{a)}$	$E_a^{b)}$	$(X_a, Y_a)^{a)}$	$\Delta R_{HX}^{a)}$	$\Delta R_{HH}^{a)}$
3.00	16.48	(3.30, 1.80)	0.30	0.40
2.50	14.67	(2.90, 1.80)	0.40	0.40
2.00	12.65	(2.40, 1.80)	0.40	0.40
1.80	11.82	(2.20, 1.80)	0.40	0.40
1.60	10.98	(2.00, 1.80)	0.40	0.40
1.40	9.80	(1.74, 1.74)	0.34	0.34

a) In units of bohr^{-1}. b) In units of kcal mol^{-1}.

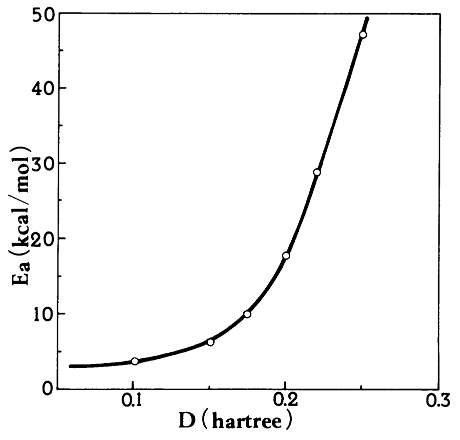


Fig. 3. The relation between the dissociation energy D and the barrier height E_a for the linear HHX system.

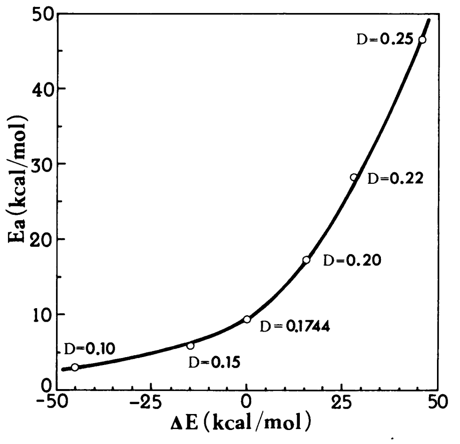


Fig. 4. The relation between the energy defect ΔE and the barrier height E_a for the linear HHX system.

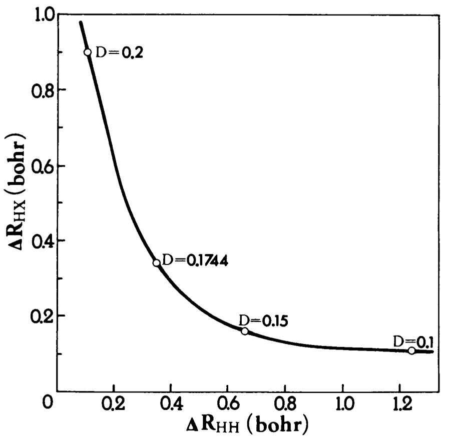


Fig. 5. The relation between the dissociation energy D and the BESP ΔR_{HX}, ΔR_{HH} for the linear HHX system.

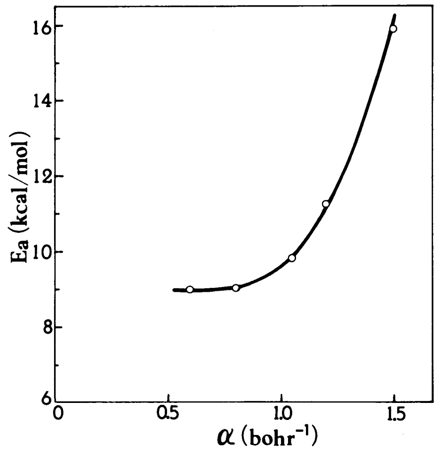


Fig. 6. The relation between range parameter α and barrier height E_a for the linear HHX system.

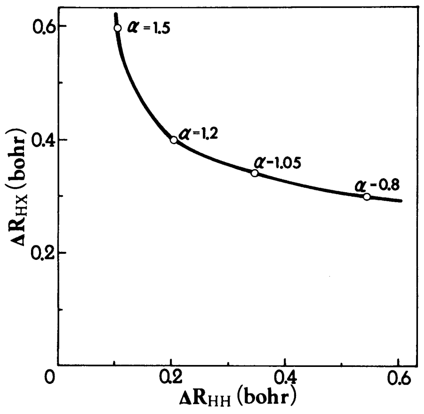


Fig. 7. The relation between the range parameter α and the BESP ΔR_{HX}, ΔR_{HH} for the linear HHX system.

where R_e is taken to be 1.40 bohr (the standard value of R_e). The energy defect ΔE of the abstraction reaction is defined as the energy difference,

$$\Delta E = E(\text{product}) - E(\text{reactant}). \quad (16)$$

By examining the energy expression of the PK or MT method, it is readily found that

$$E(\text{product}) = -D(\text{H-H}),\ E(\text{reactant}) = -D(\text{H-X}), \quad (17)$$

i.e., ΔE is equal to the difference of the diatomic dissociation energies, D(H–X)–D(H–H). The values of ΔE computed from this relation is also included in Table 1. Table 2 is a table similar to Table 1 but corresponds to Figs. 2(c) and 2(d), and Table 3 corresponds to Figs. 2(e) and 2(f). Also these interesting relations between two sets of quantities presented in Tables 1 and 2 are displayed graphically in Figs. 3—7. For example, Table 2 and Figs. 6 and 7 indicate how the height and location of the barrier change as the range parameter α is varied, provided that the values of the rest of the parameters in Eqs. 13—15 remain the same. In the next section, these relations are used to deduce the features of the PES for a series of linear abstraction reactions, H+HX=

HH+X with X=F, Cl, Br, and I.

PES of the Abstraction Reactions H+HX with X=F, Cl, Br, and I: So far the heteroatom X has not been specified. *In this section, we turn to the special case in* which X is a halogen atom. This case is of particular interest in relation to the abstraction reaction H+HX=HH+X (X=F, Cl, Br, and I), which are prototypical gaseous elementary reactions and have been the subject of numerous experimental and theoretical investigations.

To proceed in line with the considerations in the preceding section, we need the diatomic constants of the H–X molecules. They are tabulated in Table 4, where theoretical values from ab initio calculations together with some experimental values are given; the former values agree with the latter ones considerably well. We mainly confine our attention to the effect of chaging D(H–X) in the following. Thus, by using the D vs. E_a and the D vs. BESP curves in Figs. 3 and 5 together with the values of D in Table 4, the E_a and BESP for the H–H–X PES are estimated, and the result is tabulated in Table 5, which also includes the values of energy defect ΔE computed by using the relations Eqs. 16 and 17 together with the experimental D values in Table 4.

Table 4. Diatomic Constants of the HX (X=F, C, Br, I) Molecules

	H_2	HF	HCl	HBr	HI
D/hartree					
Ab initio[a]	0.1744	0.2256	0.1701	0.1447	0.1181
Exptl[b]	0.1749	0.2242	0.1714	0.1500	0.1297
α/bohr^{-1}[a]	1.050	1.181	0.989	0.958	0.913
R_e/bohr					
Ab initio[a]	1.401	1.733	2.410	2.684	3.043
Exptl[b]	1.400	1.733	2.410	2.672	3.041

a) Ref. 21. b) Ref. 23.

Table 5. Barrier Height E_a, Energy Defect ΔE and BESP ΔR_{HX}, ΔR_{HH} Obtained from the Present Calculation for the H+HX Abstraction Reactions

	$H+H_2$	H+HF	H+HCl	H+HBr	H+HI
E_a/kcal mol^{-1}	9.80	32.5	9.3	6.2	4.4
ΔE/kcal mol^{-1}		30.8	−2.2	−15.6	−28.4
ΔR_{HX}/bohr	0.34	1.0	0.3	0.15	0.1
ΔR_{HH}/bohr	0.34	0.1	0.4	0.60	1.0

In recent years, a good knowledge of the PES of the H–H–X systems (X=F, Cl, Br, and I), i.e., those of the abstraction reactions, H+HX=HH+X, has been obtained from ab initio theoretical calculations. Table 6 lists theoretical values relating to the H–H–X PES, calculated by Dunning[21,22] together with experimental values of E_a and ΔE for these abstraction reactions. Comparing Table 5 with Table 6, we find the simple calculations of the present paper lead to results in surprisingly good agreement with those from ab initio calculations. Finally Figs. 8 and 9 are plots similar to Figs. 3 and 5, but are based on the numerical values in Table 6. Again we observe that Figs. 3 and 5 resulting from the present calculation bear a very close resemblance, qualitative and quantitative, to Figs. 8 and 9 obtained from Dunning's ab initio calculation.

Since the early work of Evans and Polanyi,[25] the energetics of the reactions has been discussed by several authors.[26–30] The central point of the arguments may be understood in terms of the relations between the exoergicity and the schematic one-dimensional potential profile of the reaction. Let us start with the case X=I; as pointed out above the molecule HI has the smallest D value in Table 4, i.e., the energy of its bond being broken is smallest. Since $D(\text{H–X}) < D(\text{H–H})$, in this case, the reactant valley is shallower than the product valley, and hence $\Delta E<0$ (Table 5); in other words, the abstraction reaction H+HI is exothermic. In this connection the following propensity rules has often been argued: In the case of X=I, where the

Table 6. Theoretical and Experimental Barrier Height E_a, Energy Defect ΔE, Saddle Point Location (X_a, Y_a), and BESP ΔR_{HX}, ΔR_{HH} for the H+HX Abstraction Reactions

	$H+H_2$	H+HF	H+HCl	H+HBr	H+HI
E_a/kcal mol^{-1}					
Ab initio[a]	9.802	31.4	7.3	3.8	2.3
Exptl[b]		33	4	1.5	0
ΔE/kcal mol^{-1}					
Ab initio[a]		24.9	−5.6	−18.3	−29.6
Exptl[b]		30.8	−2.2	−15.6	−28.3
X_a/bohr[a]	1.757	1.493	1.909	2.381	2.759
Y_a	1.757	2.665	2.702	2.816	3.156
ΔR_{HX}/bohr[a]	0.357	0.932	0.292	0.132	0.113
ΔR_{HH}	0.357	0.093	0.509	0.981	1.359

a) Ref. 21. b) Refs. 22 and 24.

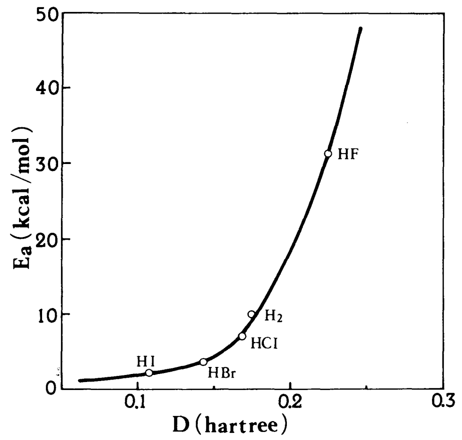


Fig. 8. The relation between the dissociation energy D and the barrier height E_a for the abstraction reactions H+HX (X=F, Cl, Br, I).

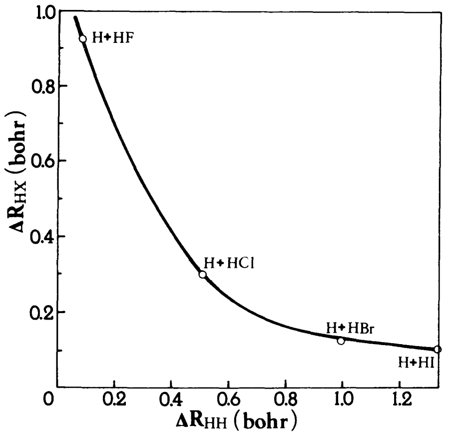


Fig. 9. The BESP ΔR_{HX}, ΔR_{HH} for the abstraction reactions H+HX (X=F, Cl, Br, I).

reactant valley is shallow, the reaction has an "early" potential barrier[31] and the barrier height E_a is rather small, but on going from X=I to X=Br, Cl, and F or, in other words, as the depth of the reactant valley D(H–X) increases, the barrier shifts to the direction of the product valley (shifts towards a "late" position) and the barrier height increases. Although these rules have been suggested by Mok and Polanyi[28] (based on the LEPS and BEBO[26] method), they have been corroborated by Dunning's ab initio calculation (Figs. 8 and 9), and also by the present calculation (Figs. 2, 3, and 5).

Finally, the problem or whether a reaction has an early or late barrier is interesting in connection with reaction dynamics. It has been deduced from molecular dynamics studies that vibrational (translational) energy excitation is effective for enhancing the rate of a reaction having a late (early) barrier.[32] It is interesting to note that the reverse reactions of the above abstraction reaction, i.e., X+HH=HX+H have been found to be enhanced by vibrational excitation when X=Cl, Br, or I, and furthermore the degree of the enhancement has been found to be in the order of Cl<Br<I.[33] This fact is in agreement with the calculated values of BESP given in Tables 5 and 6. (Remember that the PES of the reverse reactions are obtained from those of the abstraction reactions by interchanging the entrance and exit valleys.)

Conclusion

In the present paper, by using a simple semiempirical method devised by the present author and called the MT method, the PES for the linear H–H–H and H–H–X systems (the standard and reference PES) have been obtained. Referring to these PES, PES and energetics of the abstration reactions, H+HX=HH+X with X=F, Cl, Br, and I, have been discussed. Conclusions arrived at are in good agreement with those from ab initio quantum mechanical calculations. Although the treatment of the present paper is limited to the linear H–H–X system, the applicability of the MT method is wider as shown in previous paper by the author. Therefore, there are possibilities of extending the method of the present paper to treatment of, for example, systems of X–Y–Z type, or systems consisting of four or more atoms. This problem will be discussed in a forthcoming paper.

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