Location of Energy Barriers. II. Correlation with Barrier Height

M. H. Mok and J. C. Polanyi
Department of Chemistry, University of Toronto, Toronto, Canada
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In Paper I of this series a hypothetical potential-energy surface was used in order to examine the effect on the dynamics of exchange reactions \(A + BC \rightarrow AB + C\) of moving the energy barrier from an “early” to a “late” position along the reaction coordinate (i.e., from the entrance valley to the exit valley of the energy surface). In the present work an attempt has been made to correlate barrier location with other properties of the energy surface, as a step toward the application of the generalizations of Paper I to real cases. Related families of reactions have been examined in the London–Eyring–Polanyi–Sato (LEPS) and bond-energy bond-order (BEBO) approximations. The principal generalizations may be summarized as follows: (1) For substantially exothermic reactions the barrier is in the entrance valley, and for substantially endothermic reactions the barrier is in the exit valley. In the light of Paper I this implies that the cross sections for these exothermic reactions will rise most steeply with increasing translational energy in the reagents, whereas the cross sections for the endothermic reactions will rise most steeply with increasing vibrational energy in the bond under attack. (2) For decreasing barrier height in related exothermic reactions the barrier moves to successively earlier positions along the entrance valley, with increasing percentage “attractive energy release.” (3) In general [i.e., if (4), below, is obeyed even qualitatively], for increasing barrier height in related endothermic reactions the barrier moves to successively later positions along the exit valley. (4) The correlation between the classical barrier height \(E_C\) and reaction energy \(q_0\), written \(\Delta E_C = -q_0\), by Ogg and Polanyi (OP) was found to be a weaker correlation than (2), above. For families where barrier height did increase with decreasing reaction energy, a logarithmic relationship, \(\Delta \log E_C = -q_0\), was preferable for the exothermic reactions. The same relationship encompassed members of the family with \(q_0 < 0\) (endothermic reactions). With the proviso that (4) shall be applicable, (1)–(3) are summarized in the proposition that the barrier moves to successively later positions along the reaction coordinate with increasing barrier height. This progressive shift of the barrier is embodied in the following approximate relationships: \(\Delta \log E_C = -\beta q_0 \Delta \tau^2\); \(\Delta \log E_C = -\beta q_0 \Delta \tau^2 + C [q_0 \Delta \tau^2 - ]\), where \(\Delta \tau^2\) and \(q_0\) are the extensions of \(AB\) and \(BC\), from their equilibrium separation, at the crest of the barrier. In view of (4), \(\Delta \tau^2 = (\beta q_0 / \alpha) \Delta \tau^2\), a relationship which encompasses both exothermic and endothermic reactions. The fraction of attractive energy release alters from one exothermic reaction to the next by approximately \(\Delta (\alpha) = \gamma \Delta \tau^2\); hence, \(\Delta \log E_C = -q_0 \Delta (\alpha)\).

I. INTRODUCTION

In Paper I of this series we have examined the effect on the dynamics of reactions \(A + BC \rightarrow AB + C\) of a shift in the energy barrier from the entrance valley of the potential energy surface (i.e., from “surface I”) to the exit valley (“surface II”). A purely hypothetical potential energy surface was used in this study. The most striking effect of the change from surface I to surface II was to replace relative translation of the reagents as the form of energy required for barrier crossing by vibration in the molecule under attack.

In the present work we have attempted to link these hypothetical alternative situations to energy surfaces which are likely to apply in real cases. For this purpose we have calculated the characteristics of a considerable number of potential-energy surfaces, paying particular attention to the nature of changes in these surfaces on passing from member to member of a related family of reactions since, due to cancellation of errors, it is likely to be easier to obtain the direction and approxi-

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2 M. H. Mok and J. C. Polanyi, “Location of Energy Barriers. III. Effect on the Dynamics of Reactions AB + CD \rightarrow AC + BD.” J. Chem. Phys. (to be published), will examine the effect of barrier location on the dynamics of bimolecular exchange reactions AB + CD \rightarrow AC + BD.
acancy should occur at an extended \( AB \) separation, but with \( BC \) still at its normal equilibrium separation.\(^6\) This situation resembles that of surface I above. For endothermic reactions the converse situation (surface II) was applicable. A numerical calculation, in a different approximation, on the \( \text{HCl} \rightarrow \text{HCl} + \text{Cl} \) reaction, supported the view that for reaction in the exothermic direction the barrier was at an extended \( \text{H} \cdots \text{Cl} \) separation (surface I).\(^7\) The conclusion was therefore drawn that exothermic reactions would in general lead to the efficient formation of vibrationally excited products since the energy release would occur for the most part along the coordinate of approach.\(^8\) It was further concluded that the rates of endothermic reactions would be enhanced by the presence of vibration in the bond under attack, and that (due to the slowness of energy transfer into the vibrational mode) this would lead in many cases\(^7\) to a dependence of the rate of endothermic gas reactions on total pressure.\(^8\)

In later work\(^9\) it was found that, for the majority of reagent mass combinations, even if the energy release as \( A \) approached \( B \) (termed the “attractive” energy release) was only in the region of 10\% of the total energy, upwards of 70\% of the energy of reaction appeared as vibration in the \( AB \) bond. (This was explained in terms of a pattern of atomic motion which made possible what was described as “mixed” energy release.) The exceptions were reactions embodying the “light-atom anomaly”;\(^10\) i.e., reactions in which the attacking atom was much lighter than the molecule under attack. It follows that in most cases the shift of the energy barrier into the approach coordinate need not constitute a major shift in order to validate the conclusions for exothermic reactions, described above.

Several theoretical developments over the past decade prompt a re-examination of the question of barrier location. Notable among these were the development of the Sato\(^11\) modification of the London–Eyring–Polanyi\(^11\) potential-energy function (abbreviated to the LEPS function), and the discovery of the bond-energy bond-order (BEBO) method by Johnston and co-workers.\(^12\) We shall make extensive use of the LEPS and BEBO approximations in this work.

The LEPS method permits the construction of potential-energy hypersurfaces for any three-atom reaction. These surfaces provide a smooth interpolation between the Morse curve for the molecular reagent and that for the molecular product. Even after the barrier height is selected there remain further adjustable parameters that can be used to alter the barrier location. Once these fundamental parameters are chosen, changes within a related family of reactions can be simulated by changing the spectroscopic parameters entering into the Morse functions.

The BEBO method was designed for hydrogen-atom transfer reactions. It permits calculation of the potential-energy change along a single collinear minimum-energy path leading from reagent to product (it does not permit calculation of the collinear potential-energy surface). In common with the LEPS method it makes use of spectroscopic data for the pairs of atoms. There are no adjustable parameters. The method has been used extensively by Johnston, who noted that it led to the result that “the order of the bond being formed at the maximum is less than 0.5 for exothermic reactions and more than 0.5 for endothermic reactions.”\(^13\) (The “order” referred to is the Pauling bond order, and the “maximum” is the crest of the energy barrier.) It follows that, in the BEBO approximation, for exothermic \( H \)-atom transfer reactions the new bond is more extended than the old, in qualitative accord with the prediction from the simple valence bond argument referred to above. However, this aspect of BEBO theory has not been explored, since there has been little interest in barrier location.\(^13\)

In the following sections we shall use the LEPS and BEBO approximations as a means to obtaining a new correlation between barrier location and barrier height.

\(^{13}\) Since this was written we have learned of several independent studies concerned with barrier location. Marcus [R. A. Marcus, J. Phys. Chem. 72, 891 (1968); A. O. Cohen and R. A. Marcus, J. Phys. Chem. 72, 4249 (1968); R. A. Marcus (private communication)] has used the BEBO approximation to relate the bond order to the position of the barrier along the reaction coordinate. In general, smaller \( \alpha \) correlates with an earlier barrier and with larger free-energy release \(-\Delta F\). Light and Rankin [C. C. Rankin, Ph.D. thesis, Chicago University, 1968; J. C. Light (private communication)] give an example of a systematic shift in the location of a barrier to earlier positions along the reaction coordinate with increasing attractive energy release. M. Karplus and K. Morokuma (private communication) have made a numerical study of the applicability of absolute rate theory to a potential energy surface with its barrier in the entry or in the exit valley.
in related families of reactions. This marks a change of emphasis from earlier work in which we regarded barrier location and reaction energy (exothermicity or endothermicity) as the prime quantities to be linked.\(^5\) This latter correlation will also be investigated in the present work, but it will be shown to be less general than that between barrier location and barrier height. We shall re-examine the Ogg–Polanyi\(^{14,15}\) relation between barrier height and exothermicity, and shall propose a formulation which represents an improvement for exothermic reactions and which, in addition, permits the relation to be applied to endothermic members of the same homologous series. A further correlation which we shall examine is that between barrier location and percentage attractive energy release. This correlation has not previously been examined, though it was implied by the argument of Ref. 3, and more explicitly in a discussion of the effect of barrier location on product repulsion, and hence on stripping threshold energy.\(^{16}\) The question of stripping threshold energy is the subject of some discussion in Sec. IV of the present paper.

Fig. 1. Barrier height \(E_C\) versus the extension in the new bond \((r_1^b)^0=r_1^a−r_2^b\) at the crest of the barrier, for five groups of London–Eyring–Polanyi–Sato (LEPS) surfaces. (i) \(\Box\), in order of increasing \(r_1^b\), the constants were those for surfaces 6, 1, 7, 2, 8, and 3 of Ref. 9. (ii) \(\square\), in order of increasing \(r_1^b\) the constants were \(a=b=0.12\); \(c=0.30\); \(a=b=0.12\); \(c=0.40\); \(a=b=c=0.17\); \(a=0.12\); \(b=0.30\); \(c=0.40\). (iii) \(\triangle\), \(a=b=c=0.17\), throughout. (iv) \(\bigcirc\), \(a=b=0\); \(c=0\), throughout.

**II. BARRIER LOCATION ACCORDING TO THE LEPS METHOD**

The London–Eyring–Polanyi–Sato\(^{10,11}\) (LEPS) potential-energy surface has frequently been applied to the study of exchange reactions, \(A+BC→AB+C\). It provides a function \(E(r_1, r_2, r_3)\) (where \(r\) is internuclear separation; \(r_1=r_{AB}\); \(r_2=r_{BC}\); \(r_3=r_{AC}\)) for interpolation between the Morse curve of reagent BC, \(E(r_{BC})\), and that of product AB, \(E(r_{AB})\). An extended LEPS equation introduces further flexibility into the expression.\(^{17}\)

In Ref. 9 a study was made of extended LEPS surfaces that bore some resemblance (through the choice of spectroscopic constants) to the surface appropriate to the exothermic reaction \(H+Cl→HCl+Cl\). Within this loose restriction, the constants governing the extended LEPS equation were varied quite freely. Nonetheless, there was evidence of a negative correlation between the height of the barrier and the extension of the new bond at the crest of the barrier.

This is shown in Fig. 1 as a correlation between \(E_C\) and \(r_1^b\), the former quantity being the classical barrier height (without inclusion of zero-point energies), and the latter being defined as the separation between the crest of the barrier and the equilibrium distance in the new bond, i.e., \(r_1^b=r_1^a−r_2^b\). The potential-energy surfaces in question have been designated as family (i) in the figure. They constituted a "family" in this case only through the fact that the spectroscopic constants for the most part were those for \(H+Cl\); however, no attempt was made to vary the remaining parameters.


\(^{15}\) M. G. Evans and M. Polanyi, Trans. Faraday Soc. 34, 11 (1938).


systematically. The surfaces do not, therefore, correspond to a homologous series of reactions. The correlation is correspondingly poor. It is, nevertheless, quite evident.

A positive correlation can also be seen to exist in this group of exothermic reactions between the percentage of the energy release along the coordinate \( r_1 \) and the magnitude of the displacement of the crest of the energy barrier along \( r_1 \). This is shown in Fig. 2 ["family" (i)], where the percentage of attractive energy release\(^{18} (\alpha_A) \) is plotted against \( r_1 \).

A second group of LEPS surfaces was obtained using the correct spectroscopic constants for the exothermic exchange reaction \( \text{Cl}+\text{HI} \rightarrow \text{HCl}+\text{I} \). These surfaces were generated in exploratory work for a Monte Carlo study of this system.\(^{18} \) Once again the variation in constants was not systematic, and the group does not correspond to a homologous series. Nonetheless the correlations between \( E_C \) and \( r_1 \), and between \( (\alpha_A) \) and \( r_1 \), are clearly evident in Figs. 1 and 2 ["family" (ii)].

The three other groups of LEPS surfaces examined did resemble homologous series of reactions. Within each group the adjustable constants \( a, b, \) and \( c \) were held constant (the values are shown in Fig. 1). The only changes made from member to member of the series were changes in the spectroscopic constants (and hence reaction energy) from those appropriate to one reaction to those appropriate to some closely related reaction. No ad hoc adjustments were made in the spectroscopic constants. Groups (iii) and (iii)\(^{19} \) included all members of the series \( \text{Cl}+\text{HX} \rightarrow \text{HCl}+\text{X} \), where \( \text{X} = \text{F}, \text{Cl}, \text{Br}, \) and I. Data for series (iii) and (iii)\(^{19} \) are shown in Figs. 1 and 2. (The first member, \( \text{Cl}+\text{HF} \), is endothermic. As will be shown in Fig. 4, the crest of the energy barrier is in the exit valley of the potential-energy surface; consequently, in Fig. 1 we would have

\(^{18} (a) \) In the simplest case the attractive energy release \( \alpha_A \) is the energy released as \( r_1 \) is changed from \( r_1 = 0 \) to \( r_1 = r_2 \), on the collinear potential-energy surface. Hence \( (\alpha_A) = \left[ \frac{1}{2}E_C + a \right] \times 100\% \), with \( a = -\Delta E_C \). If there is a barrier in the entry valley of the collinear surface, then \( \alpha_A \) is given by the energy released in going from the crest of the barrier to \( r_2 \). If the route along \( r_1 \) from \( r_1 = 0 \) to \( r_1 = r_2 \), or (where a barrier is present) from \( r_1 = r_1 \) to \( r_1 = r_2 \), encounters a change from attractive to repulsive force, then at the point where the attractive force (downward sloping entry valley) gives way to repulsive force the attractive energy release is doomed to fail. If we call this point \( r_2 \) (since "core repulsion" has set in), then the value of \( \alpha_A \) in such a case is the energy released as \( r_1 = 0 \) goes to \( r_1 = r_2 \), or (where a barrier is present) as \( r_1 = r_1 \) goes to \( r_1 = r_2 \); (b) Since the BEBO method does not lead to a potential energy surface, but to an energy profile along the reaction coordinate, we have obtained the repulsive energy release \( (\alpha_A) \) of the surface \( \alpha_A \) by the procedure previously developed\(^{18} \) for the analysis of collinear trajectories. The repulsive energy release was defined\(^{18} \) as the energy released after \( r_1 \) became equal to the normal amplitude of \( A_B \) at 300 \( \text{K} \). Hence \( (\alpha_A) = \left[ \frac{1}{2}E_C + a \right] \times 100\% \). We did not distinguish attractive from mixed energy release\(^{4} \), but simply equated \( (\alpha_A) = 100\% - (\alpha_A) \).


for this reaction \( r_1^{1.0} \approx 0, r_1^{1.0} \) being the interesting quantity.) In order of increasing \( r_1^{1.0} \), \( X = \text{Cl}, \text{Br}, \) and I in groups (iii) (closed triangles) and (iii) (open triangles) of Fig. 1. Group (iv) included all members of the family \( \text{H}+\text{X} \rightarrow \text{H}+\text{X} \), where \( X = \text{F}, \text{Cl}, \text{Br}, \) and I. All the members of this series are shown in Figs. 1 and 2. In order of increasing \( r_1^{1.0} \), \( X = \text{Cl}, \text{Br}, \text{I}, \) and \( \text{F} \). For all three groups, (iii), (iii), and (iv), the correlation between \( E_C \) and \( r_1^{1.0} \) and between \( (\alpha_A) \) and \( r_1^{1.0} \) is clear.

There is evidence that the LEPS surfaces used for families (iii) and (iv) are of roughly the right form. A detailed Monte Carlo study has been made of the classical dynamics of the reaction \( \text{Cl}+\text{HI} \) proceeding on an energy surface which resembled that used for family (iii).\(^{19} \) (The only difference was in the constant \( \beta_{\text{HCl}} \), which was reduced in the Monte Carlo calculation to 0.8 times its spectroscopic value, in order to increase the reactive cross section.) The Monte Carlo calculation indicated that an energy surface with \( (\alpha_A) \approx 24\% \) was required in order to account for the experimental product energy distribution. The surface used for \( \text{Cl}+\text{HI} \) in family (iii) had \( (\alpha_A) = 16\% \), in reasonable agreement with this requirement. The barrier height for \( \text{Cl}+\text{HI} \) in family (iii) was \( E_C = 0.25 \) kcal mole\(^{-1} \). There is no direct experimental measurement of \( E_C \) for this reaction, but judging by the ease with which infrared chemiluminescence can be observed at low pressure from this system, it appears that \( E_C \leq 2 \) kcal mole\(^{-1} \). For \( \text{Cl}+\text{HCl} \) in family (iii) \( E_C = 3.26 \) kcal mole\(^{-1} \), as compared with the experimental value of \( E_C \approx 6.5 \) kcal mole\(^{-1} \).

The set of LEPS surfaces designated (iii)\(^{19} \) also made use of the spectroscopic constants for the four reactions \( \text{Cl}+\text{HX} \). They differed from (iii) in the choice of the constants \( a, b, \) and \( c \) (see the caption to Fig. 1). The values of \( a, b, \) and \( c \) used for (iii)\(^{19} \) produced surfaces with a smaller range of barrier heights (Fig. 1) but larger range of \( (\alpha_A) \) (Fig. 2) than in (iii). Though (iii)\(^{19} \) gave a poorer approximation to the actual interactions in the \( \text{Cl}+\text{HX} \) family, it was nonetheless of interest to examine the effect on the correlations \[ E_C \text{ vs } r_1^{1.0}, (\alpha_A) \text{ vs } r_1^{1.0}, \text{ and } E_C \text{ vs } q_0 \] of a change in the range of \( E_C \) and \( (\alpha_A) \) encompassed by the family.

For the reactions \( \text{H}+\text{Cl}_2 \) and \( \text{H}+\text{Br}_2 \) in family (iv) \( (\text{H}+\text{X}) \) there is evidence that the LEPS equation used here is, once again, in rough accord with experiment [see especially footnote 5 of Ref. 19(a)]. The equation predicts an activation barrier of \( E_C = 2.4 \) kcal mole\(^{-1} \) for the collinear approach of \( \text{H}+\text{Cl}_2 \), and \( E_C = 1.8 \) kcal mole\(^{-1} \) for collinear approach in \( \text{H}+\text{Br}_2 \). The experimental activation energies are in the region of \( E_C \approx 2.0 \pm 0.5 \) kcal mole\(^{-1} \) for \( \text{H}+\text{Cl}_2 \) and \( E_C \approx 1.2 \pm 0.5 \) kcal mole\(^{-1} \).
mole$^{-1}$ for H$+$Br$_2$. The percentage attractive energy release predicted by the family (iv) LEPS surfaces for H$+$Cl$_2$ is (a$_1$) $= 37\%$, and for H$+$Br$_2$ (a$_1$) $= 42\%$. The experimental product energy distribution requires for H$+$Cl$_2$ (a$_1$) $= 20\%–30\%$, and for H$+$Br$_2$ (a$_1$) $= 30\%–40\%$, in rough agreement with the family (iv) surfaces.

In the light of this evidence for the reasonableness of the LEPS energy surfaces for families (iii) and (iv), we present the data recorded in Figs. 1 and 2 in a semiquantitative form through the approximate empirical relationships

\[
\Delta E_C = -\beta_1 \Delta r_{1,0} \tag{1a}
\]

and

\[
\Delta(a_1) = \gamma_1 \Delta r_{1,0} \tag{2a}
\]

These relationships are applicable to the exothermic members of the series (including the thermoneutral reaction, Cl$+$HCl, as a limiting case). In family (iii) (Cl$+$HX) the least-squares values of the constants were $\beta_1 = 3.4$ kcal mole$^{-1}$Å and $\gamma_1 = 32$ Å$^{-1}$. In family (iii'), $\beta_1 = 1.3$ kcal mole$^{-1}$Å and $\gamma_1 = 110$ Å$^{-1}$. In family (iv) the values were $\beta_1 = 5.3$ kcal mole$^{-1}$Å and $\gamma_1 = 169$ Å$^{-1}$.

From (1) and (2) it follows that there is an approximate negative correlation between the activation energy (as given by $E_C$) and the percentage of attractive energy release in related series of reactions of the form

\[
\Delta E_C = -(\beta_1 / \gamma_1) \Delta(a_1). \tag{3}
\]

The proportionality constant $\beta_1 / \gamma_1$ was 0.1 kcal mole$^{-1}$ for (iii), 0.01 kcal mole$^{-1}$ for (iii'), and 0.03 kcal mole$^{-1}$ for (iv).

For exothermic reactions it was found that $r_{1,0}$ was significant, but $r_{1,0}$ was small. This was indicative of the fact that the barrier was in the entrance valley of the energy surface. For all those reactions in Fig. 1 for which $r_{1,0} > 0.7$ Å, $r_2 < 0.1$ Å; usually $r_{1,0} < 0.1$ Å ($\sim 0.01$ Å). There was in all cases a rough inverse relationship between $r_{1,0}$ and $r_{2,0}$. For the homologous series (iii) and (iii'), which covered a large range of $r_{1,0}$ extending from $\sim 0.2$ Å for Cl$+$HCl to $\sim 1.3$ Å for Cl$+$HI, this could be represented as a roughly logarithmic relationship

\[
\Delta \log r_{1,0} = -a \Delta r_{1,0}, \tag{4}
\]

embracing the exothermic and thermoneutral members of the families. The relationship did not, however, apply to the family exemplified in (iv), in which both atoms B and C were changed from member to member. The values of the constants were for (iii) $a = 1.36$, and for (iii') $a = 0.69$. The largest value of $r_{1,0}$ (0.155 Å) among the exothermic and thermoneutral reactions

22 These percentages will be known more precisely when Monte Carlo calculations on these two reactions (currently under way) are completed.

(iii) and (iii') corresponded to the smallest value of $r_{1,0}$ (0.185 Å), these being the values for the thermoneutral member of group (iii), Cl$+$HCl. The fact that $r_{1,0} \approx r_{2,0}$ for this example is also evident in the top graph of Fig. 4. The inverse relationship between $\Delta \log r_{1,0}$ and $\Delta r_{1,0}$ of Eq. (4) implies the following relation between extension of the old bond at the crest of the barrier and the barrier height of related exothermic reactions:

\[
\Delta E_C = \beta_1 \Delta \log r_{1,0}, \tag{1b}
\]

where $\beta_1 = \beta_1 / a$. Similarly, the extension of the old bond at the crest of the barrier can be linked to the percentage attractive energy release,

\[
\Delta(a_1) = -\gamma_1 \Delta \log r_{1,0}, \tag{2b}
\]

where $\gamma_1 = \gamma_1 / a$.

The reverse of all the exothermic reactions discussed in this section constitute examples of endothermic reactions. Equations analogous to (1a) and (1b) can be written for these endothermic reactions. In the discussion that follows it will be convenient to refer to the reverse (endothermic) reactions as C$+$BA$\rightarrow$CB$+$A, the reagents being redefined as C$+$BA, the products as CB$+$A. We wish, nonetheless, to retain the convention that $r_1$ represents the coordinate along which the reagents approach, $r_2$ the coordinate along which the products separate. We therefore interchange the definitions of $r_1$ and $r_2$ in discussing these related families of exclusively endothermic reactions. Barriers that were described as being in the entry valley $r_1$ of the exothermic energy surfaces are now described as being in the exit valley $r_2$ of the endothermic energy surfaces. This requires for the endothermic reactions C$+$BA that $r_1 \equiv r_{BC}$, $r_2 \equiv r_{AB}$, the definition of $r_5$ remaining unchanged.

The activation energy $E_C'$ in the endothermic direction is given by the heat of reaction in the exothermic direction $q_r$ plus the barrier height in the exothermic direction, i.e., $E_C' = q_r + E_C$. The quantity $q_r$ denotes the energy of the reagents minus the energy of the products, without inclusion of zero-point energy; $q_r > 0$ for exothermic reaction. For a related series of endothermic reactions (including thermoneutral reaction, as a limiting case), the important relation (1a) becomes

\[
\Delta E_C' - q_r = -\beta_1 \Delta r_{1,0} \text{ ENDO} \tag{1a'}
\]

since the left-hand side is $E_C$. The relationship says that for reaction in the endothermic direction the extension of the bond being broken at the crest of the barrier increases approximately linearly with decreasing barrier height for the reverse (exothermic) reaction. In cases where the Ogg-Polanyi (OP) relationship

\[
\Delta E_C = -\alpha q_r \tag{5}
\]

is applicable in the exothermic direction, Eq. (1a') for
the endothermic reaction reduces to

$$\Delta q_e = (\beta f/\alpha) (\Delta r^2)^{\text{ENDO}}. \quad (1a'')$$

Both $\alpha$ and $\beta$ are positive. In the common case that the OP relationship is applicable, $(1a'')$ predicts that for related endothermic reactions the extension of the bond at the crest of the barrier will increase approximately linearly with increasing absolute value of the reaction energy.

The value of $\alpha$ in (5) is known to be $0<\alpha<1$; typically $\alpha \approx 0.2-0.3$. Consequently, $|\Delta q_e| > |\Delta E_c|$. Hence in $\Delta E_c' = \Delta E_c + \Delta q_e$, $\Delta E_c'$ has the same sign as $\Delta q_e$. Consequently, from $(1a''')$, $(\Delta r^2)^{\text{ENDO}}$ has the same sign as $\Delta E_c'$. The qualitative conclusions from $(1a)$ and $(1a'')$ can therefore be summarized as follows: For related exothermic series of reactions, Eq. $(1a')$ records the fact that with increasing barrier height the crest of the barrier moves to later locations along the coordinate of approach; i.e., $\Delta r^2$ increases. For related endothermic series, $(1a'')$ indicates that with increasing barrier height, the crest of the barrier commonly (i.e., if the OP relationship is obeyed even qualitatively) moves to later locations along the coordinate of separation; i.e., $(\Delta r^2)^{\text{ENDO}}$ increases. These qualitative relationships are illustrated pictorially in Sec. IV.

There is considerable empirical evidence for the existence of a negative correlation between activation energy $E_a$ and reaction energy $q_e$ in related series of exothermic reactions. This was interpreted by Ogg and Polanyi in terms of Eq. (5), which was proposed for related series of exothermic exchange reactions in which the rejected atom or group was changed systematically, or for a series in which the attacking atom or group was changed. It has been tested most extensively for the first case. We shall refer to the first type of homologous series as "family C" since in $A+BC \rightarrow AB+C$ it is $C$ (and only $C$) that is varied from member to member of the family. The second type of series to which (5) may apply we shall call "family A." It was not expected that (5) would be applicable to "family B," nor to mixed families (families "AB," "BC," or "AC," in which both of the designated species are changed).

The reactions in group (iii) and (iii'), Cl+HX, belong to family C. Figure 3 suggests that there may be an approximately linear relationship between $E_c$ and $q_e$, so long as the barrier heights are small, that is to say, so long as the barriers are all well out in the entry valley of the surface. For family (iii') even the thermoneutral member of the Cl+HX family, Cl+HCl, falls within the roughly linear region. Significantly, Cl+HCl has $r=0.73$ Å in (iii'), i.e., it well into the entry valley [in contrast to Cl+HCl according to the approximation of family (iii); Fig. 4]. The slope of the linear relationship for family (iii') is, however, $\alpha=0.023$, an order of magnitude less than the figure normally encountered (cf. Sec. III).

Figure 4 illustrates the various findings for the four members of the Cl+HX family, in approximations (iii) and (iii'), by showing the potential-energy profile along the reaction coordinate. It includes potential-energy profiles for family (iv), H+XX. The reaction coordinate is taken to be the path of lowest energy across the collinear potential-energy surface. Reaction proceeds from left to right, with the reagent energy taken as zero in each case. The trip along the reaction coordinate begins at a fixed value of the initial separation $r_1=4.7$ Å in each of the three families pictured. For $A=Cl$ and $B=H$ [or vice versa—see family (iv)] this corresponds to an initial separation $r=6.0$ Å. For H+XX with $X=F$, Br, and I, the reaction coordinate begins at $r=5.6$, 6.1, and 6.3 Å, respectively. Distance along the reaction coordinate was symbolized $r$. Since the initial separation of the bond being formed was 4.7 Å in every case, the "corner" of the reaction path, for which $r_1-r_0=r_2-r_3$, was reached at $r=4.6$ Å; more precisely, at a value of $r$ in the range $r=4.4-4.7$ Å. This point along the reaction coordinate, where the entry valley may be said to give way to the exit valley, is indicated in Fig. 4.

For the Cl+HX family in approximations (iii) and (iii') it is clear that (a) as the barrier height increases the crest of the barrier moves to successively later locations along the reaction coordinate (as shown from a different standpoint in Fig. 1), (b) for the substantially endothermic reaction Cl+HF the barrier is located in the exit valley of the surface, whereas for the substantially exothermic reaction Cl+HI it is located.
in the entry valley of the surface, (c) for exothermic reactions, as the barrier moves to earlier locations in the entry valley the percentage of the energy release that takes place in that valley, i.e., the percentage of attractive energy release, increases, and (d) as the exothermicity increases the barrier falls.

The reactions in group (iv), H+X₂, differ from one another in the nature of both atoms B and C (the family is of type BC). There is no rationale in such a case for the OP relationship of Eq. (5), nor does such a relationship apply. This can be seen by inspection of the energy profiles shown in Fig. 4. The energy profiles cross one another; this is indicative of the fact that lower barriers can correspond to higher potential energy along the exit valley, i.e., to smaller exothermicity. The OP relationship, therefore, fails to apply even qualitatively.

Nonetheless, the three other correlations, (a), (b), and (c) above, are clearly evident. The fact that the correlations between barrier height and barrier location, and between percentage attractive energy release and barrier location, hold when the OP relationship fails to apply even qualitatively indicates that these new relationships embody a “stronger” correlation than the OP one. This is confirmed in the following section, and is discussed in Sec. IV.

III. BARRIER LOCATION ACCORDING TO THE BEBO METHOD

Johnston and co-workers have devised an ingenious and effective empirical method for the prediction of the heights of activation barriers in exchange reactions A+HC→AH+C, where A and C may be any atoms or radicals and H is atomic hydrogen. The method, termed the bond-energy bond-order (BEBO) method, makes use of an extension of Pauling’s empirical relationship between bond energy E and bond order n. The BEBO method assumes collinear reaction, exclusively. The equation which gives the potential energy E(r₁, r₂) along the reaction coordinate, as a function of the order of the old bond nₒ, is

\[
E(r₁, r₂) = Eₐ₁(1−nₒⁿ) − E₁(1−nₒⁿ) + E₄\exp(−\beta₁)\left[1 + \frac{1}{3} \exp(−\beta₁)\right]
\]

where E₄, E₅, and E₆ are the (single) bond energies in isolated AH, HC, and AC. The exponents p and q are the powers of n in the Pauling relationships

\[
E₁ = E₄nⁿ₄
\]

Fig. 4. Energy profiles along the path of minimum energy for three families [(iii), (iii), and (iv)] of LEPS energy surfaces. The potential energy is plotted against the distance r along the minimum path, starting in every case with r=0.5 Å, corresponding to an extension of the new bond, r₁−r₂=4.2 Å. The point along the reaction coordinate at which the entry valley may be said to give way to the exit valley (r₁−r₂=4.2−r₂) is indicated by a vertical dashed line. [The two vertical dashed lines for family (iv) show limiting cases, H+H₂ at the left, and H+H₂ at the right.] Arrows indicate the crest of the energy barriers. Due to variation in the nature of the bond being broken, a given value of r corresponds to different values of r₂−r₁ for different members of the family; the range of variation is recorded on the scales. The single-line markers record the scale for the X=F member of the family, and the double-line markers the scale for X=I. The markers for Cl and Br (not shown) would lie in between, in order of increasing atomic number.

---

and

\[ E_5 = E_2 m_p^p. \]  

The third term in (6) is a modified Sato\textsuperscript{30} triplet function \([\text{the modification consisted in multiplication by a further factor of } \frac{1}{2} \text{; see page 60 of Ref. 12(c)}]; \beta \) is a spectroscopic constant.

The \( E_3 \) term in (7) gives an estimate of the bonding contribution from the partially severed \( H \cdots C \) bond, the \( E_2 \) term adds to this the bonding due to the partially formed \( A \cdots \cdot H \) bond, and the \( E_2 \) term introduces the \( A \cdots \cdot C \) repulsion. The zero of energy, as in Sec. II, corresponds to the reagent configuration, \( A+HC \) \( \text{[hence } E_0 \text{ in (7)]}. \) Consequently, as the reaction proceeds \( E_2=\equiv E_2 \) changes from zero to a positive quantity, \( -E_1 \) changes from zero to a negative quantity, and \( E_3 \) goes from zero to a positive value and then once again to zero.

The underlying concept is suggested by the spin orientations \( A \uparrow H \downarrow C \uparrow \). It is supposed that the energy of the system can be decomposed into two partial bonds and one antibond. The reaction proceeds by maximizing the bonding, while minimizing the antibonding. The latter requirement is met by keeping \( A \) and \( C \) separated through collinearity. The former requirement is embodied in the restriction \( n_1+n_2=1 \), which is used in deriving (6). Initially \( n_1=0 \) and \( n_2=1 \), and finally \( n_1=1 \) and \( n_2=0 \). It appears intuitively reasonable that \( n_1+n_2=1 \) should ensure the greatest possible total bonding.

The success of (6) testifies to the soundness of this intuition. Potential energies of activation have been calculated for 130 \( H \)-atom transfer reactions, and have been found in general (though not invariably) to agree with established activation energies to within 2 or 3 kcal.

Equation (6) was applied in the present work to seven homologous series of reactions involving hydrogen-atom transfer. Judging by the activation barriers the method succeeded as a semiquantitative tool in two of these families, and as a rough qualitative guide for three of the remaining five.\textsuperscript{24}

Families (i) to (iii) were of "type C" in which the rejected atom was the species being varied from member to member of the family. Family (i) consisted of four reactions \( H+HX \) (\( X=\text{F, Cl, Br, and I} \). Family (ii) consisted of four reactions \( H+HM \) (\( M=\text{Li, Na, K, and Rb} \). The calculated barrier heights are recorded along the ordinate of Fig. 5. For family (i) they agree quite well with experiment.\textsuperscript{30} For family (ii) there are no experimental data, but the value for \( H+\text{Li} \) appears reasonable in the light of the 9 kcal mole\textsuperscript{-1} classical barrier height for \( H+\text{H}_2 \). Family (iii) (as in the previous section) comprises the reactions \( Cl+\text{HX} \). The change in barrier height along the series is much too small, resembling that in the LEPS series (iii'). The predicted barrier height for \( Cl+\text{HCl} \) is \( E_0=0.23 \) kcal mole\textsuperscript{-1}, whereas the experimental value is \( E_0=6.5\pm 0.5 \) kcal mole\textsuperscript{-1}.\textsuperscript{30} However, the increase in barrier height in going from \( Cl+\text{HI} \) to \( Cl+\text{HCl} \) is qualitatively correct.

Families (iv) and (v) were of "type A." Since family (iv) was \( \text{X+HI} \) and (v) was \( \text{X+HBr} \), and since both of these embody reactions of the general variety \( \text{X+HY} \) \( \text{[see (iii) above]}, \) it was to be expected that the absolute values of the barrier heights would once again be unrealistically low, and would vary little from member to member of a family. Nonetheless, the qualitative picture (Fig. 6) may be correct in most respects.

Families (vi) and (vii) were \( Cl+\text{HM} \) and \( H+\text{HX} \) (types C and A, respectively). The barrier heights predicted by BEBO theory ranged from 5.4 kcal mole\textsuperscript{-1} for \( Cl+\text{HNa} \) up to 21 kcal mole\textsuperscript{-1} for \( F+\text{HK} \). These barrier heights are probably 10-100 times too high. (Experimental data are lacking, but the value of \( E_0 \) for \( F+\text{H}_2 \), which would be expected to be substantially in excess of that for \( F+\text{HK} \), is \( E_0=1.7 \) kcal mole\textsuperscript{-1}.\textsuperscript{30}) The failure of the BEBO method in this case is probably of a fundamental sort. The spectroscopic constants for an ionic bond apparently do not lend themselves to the calculation of triplet-state repulsion by way of the modified Sato prescription. We did not, therefore, attach any weight to the predictions of the BEBO method for families (vi) and (vii).

The plots of \( E_0 \) versus \( q_e \) for the three families of type C (at the left of Fig. 5) give evidence of an OP type of relationship linking the thermoneutral and the exothermic members of each family. The values of \( \alpha \) are "normal" for families (i) and (ii) (\( \alpha=0.22 \) and \( \alpha=0.11 \)) but extremely low for family (iii) (\( \alpha=0.003 \)). Family (iii), as already noted, is certainly unreliable from a quantitative standpoint.

As in the case of (iii') on the LEPS approximation of Sec. II, it is found that the closest approach to linearity of \( E_0 \) with \( q_e \) occurs when the crests of the barriers for the reactions being compared are all well out in the entrance valley of the energy surface. This is the case for the four members of the \( H+\text{HM} \) family, all of which correspond to highly exothermic reactions and all of which have \( r_\text{e}^{\text{e}^+}>0.6 \) Å.

The two families of type A (plots of \( E_0 \) versus \( q_e \) are at the left of Fig. 6) are qualitatively at variance with the OP relationship. (Note that \( I+\text{HBr} \) is endothermic; this explains its high barrier.) In the series I,
Br, Cl+HI and Br, Cl+HBr the barrier height increases with increasing exothermicity. This may well represent a qualitative failure of the BEBO method, rather than a failure of the OP relationship, since the total variation of $E_C$ in these reactions is $<\pm 0.1$ kcal mole$^{-1}$ according to the BEBO calculations.

Inspection of the second column in Figs. 5 and 6 shows in every case that $r_{1.0}$ increases with decreasing barrier height. This is true whether $E_C$ decreases with increasing exothermicity (Fig. 5) or not (Fig. 6). For the exothermic members of each family ($q_0>0$) there is an approximately linear relationship between $\Delta E_C$ and $-\Delta r_{1.0}$ of the form shown in Eq. (1a). The values of $\beta$ for the five families were (i) $\beta_1=6.3$, (ii) $\beta_1=5.9$, (iii) $\beta_1=0.11$, (iv) $\beta_1=0.4$, (v) $\beta_1=1.3$, in units of kilocalories mole$^{-1}$/angstrom. For the reasons already given, these numerical values are most likely to correspond to reality for cases (i) and (ii). Once again it is apparent that a linear relationship applies most clearly when the reactions being compared have their
barriers located well out in the entry valley of the energy surface, i.e., in the case of family (ii).

Figures 5 and 6 show that $r_{2,0}^{1.0}$ is very small for all exothermic reactions, since the barrier is in the entrance valley. As for the LEPS surfaces, for $r_{1,0}^{1.0}$ > 0.7 Å, $r_{2,0}^{1.0}$ < 0.1 Å, and usually $r_{2,0}^{1.0}$ < 0.1 Å. The inverse relationship between $r_{1,0}^{1.0}$ and $r_{2,0}^{1.0}$ for exothermic reactions noted in the previous section can be represented by Eq. (4) in all cases. The magnitude of $\alpha$ for the various families was (i) $\alpha = 1.78$, (ii) $\alpha = 1.75$, (iii) $\alpha = 1.47$, (iv) $\alpha = 1.36$, and (v) $\alpha = 1.63$.

The observation that $r_{2,0}^{1.0}$ was small was only applicable to the exothermic reactions. For endothermic reactions the inequality was reversed; $r_{2,0}^{1.0}$ > $r_{2,0}^{1.0}$ (as in the LEPS approximation, Fig. 4). The barrier had moved into the exit valley of the energy surface.

The final columns of graphs, in Figs. 5 and 6, show that in the BEBO, as in the LEPS, approximation there is a tendency for the percentage attractive energy release\(^{10}\) to increase roughly linearly with decreasing barrier height in homologous series of exothermic reactions. [The only exception is the change in family (iv) from Br+HI to F+HI.] The correlation was described in Eq. (3) of Sec. II. The values of the proportionality constants $\beta_2/\gamma_1$ from the data of Figs. 5 and 6 were (i) $\beta_2/\gamma_1 = 0.05$, (ii) $\beta_2/\gamma_1 = 0.14$, (iii) $\beta_2/\gamma_1 = 0.01$, (iv) $\beta_2/\gamma_1 = 0.02$ (ignoring F+HI), and (v) $\beta_2/\gamma_1 = 0.09$, all in kilocalories mole\(^{-1}\). The correlation, like that of Eq. (1a), is a stronger one than the OP relation of Eq. (5). The numerical values, once again, are probably only significant for cases (i) and (ii).

As in the case of the LEPS surfaces, we present energy profiles along the reaction coordinate (Fig. 7). These are given for families (i)-(iii) only, corresponding to the data of Fig. 5. The energy profiles for families (iv) and (v) can be inferred qualitatively from the plots in Fig. 6. The profiles for (i) to (iii) illustrate the negative correlation between the barrier height and the magnitude of the energy release, and also the systematic movement of the barrier crest from a position very early along the reaction coordinate in highly exothermic reactions to a position very late along the
reaction coordinate for highly endothermic reactions. The qualitative picture closely resembles that shown for the LEPS surfaces in Fig. 4.

The conclusions from this examination of five homologous series by the BEBO method are substantially the same as the conclusions from the study of five groups of energy surfaces by the LEPS method in the previous section. The approximate linear relationships between barrier height and barrier location, and also between barrier height and percentage attractive energy release, survive even when the model leads to a failure of the OP relationship. It appears, therefore, that these correlations between \( E_C \) and \( r_1^{-0.5} \) and between \( E_C \) and \( \alpha_\Lambda \) are stronger than that between \( E_C \) and \( q_C \).

IV. DISCUSSION

Of the five groups of surfaces examined in the LEPS approximation, three comprised "homologous series" of reactions. Five further homologous series were investigated with some success in the BEBO approximation. Only three of the total eight homologous series obeyed the Ogg–Polanyi (OP) relationship \( \Delta E_C = -\alpha \Delta q_\Lambda \), [Eq. (5)], even qualitatively. "The three were LEPS family (iii) and BEBO families (i) and (ii)."

In some cases this can probably be traced to a weakness in the surface. In one case [LEPS family (iv); \( H+X_L \)] the failure of the OP relationship is to be expected in view of the fact that the family is type BC, and it is probably correctly represented. In all cases the relationships (1a), (2a), and (3) put forward in the present work are at least qualitatively applicable, despite the failure of (5). The fact that (1a), (2a), and (3) embody "stronger" relationships than (5) can be understood in a qualitative way by reference to a simplified energy surface. Equation (5) was explained by Ogg, Evans, and Polanyi (OEP)\(^{14,15}\) in terms of Fig. 8(a),\(^{16}\) which they applied to reactions of the electron-switch variety \( M+XR \to M^++(XR) \to M^+X^-+R \) (M is an alkali-metal atom, \( X \) is a halogen, and \( R \) is an organic radical). The success of their relationship led to the application of the same construction to exothermic reactions in general, though it was recognized that the assumption of a "switch" in the activated state, from reagent to product electronic state, must be a very poor one.

For \( M+XR \), OEP argued that M could approach to within bonding distance of XR without incurring appreciable repulsion. The origin of the activation barrier was to be found in the necessity for extending the \( X-R \) bond in order to achieve a configuration of degeneracy with nonbonded (repelling) \( X^-R \). The crest of the barrier was, therefore, located along the coordinate of separation \( r_2 \). Figure 8(a) is an OEP potential-energy diagram. The negligible effect of the approach of M to within bonding distance of XR is indicated in Fig. 8(a) by the rise in the minimum of the B-C curve from the level of the dashed line to that of the solid line. The degeneracy at the crest of the barrier can be represented by the equality

\[
E_{B-C}(r_2) = E_{B-C}(r_2) - q_C, \tag{9}
\]

in which the left-hand side refers to an attractive B-C interaction in the reagent electronic state and the right-hand side to a repulsive B-C interaction in the product electronic state. (The true electronic wavefunction at and near the crest of the barrier would be a hybrid of these pure states, but it was hoped that changes in barrier height could be correctly represented by this zero-order approximation.) The energy on the left-hand side of Eq. (9) is reckoned relative to the reagent energy, and the term in \( E \) on the right-hand side relative to product energy.

The effect of changing the reaction energy \( q_C \) is shown in the figure, on the assumption that the func-
tional form of the \( X^- \cdot R \) repulsion remains unchanged despite the fact that the \( R \) has been replaced by \( R' \). This invariance of the functional form of the \( B \cdot C \) repulsion from reaction to reaction is an essential feature in the derivation of (5). It is a questionable assumption even for families of type \( C_1 \), and is unlikely to be correct for families of type \( BC \), e.g., family (iv) of Sec. II (\( H+X_2 \)).

The invariance of the functional form of \( B \cdot C \) repulsion does not, however, enter into Eq. (1a) of the present study. This equation describes a correlation, in related reactions, between the height of the highest point on the collinear surface and its location along the reaction coordinate. A correlation of this type is evident in the OEP pictures: as the barrier falls the crest moves to the left in the picture. (This represents a decrease in \( r_3 \), rather than an increase in \( r_1 \); the discrepancy will be eliminated when the OEP plots are redrawn; later in this discussion.) The correlation was not remarked upon by the original workers, since at that date there was little interest in features of the energy surface other than barrier height. It appears reasonable that this further correlation should be a stronger one than the OP correlation. If, for example, the \( B \cdot C \) repulsion becomes a steeper function of internuclear separation, an increase in \( q_e \) can be accompanied by an increase in \( E_{\text{C}} \), in qualitative disagreement with the OP relation. However, the increase in barrier height will, within the approximation of these simple drawings, still be accompanied by a shift in barrier location, of the proper sign. (See, however, the more detailed discussion that follows.)

The 18 LEPS potential-energy surfaces (with a wide range of constants), all corresponding to exothermic reactions, all predicted that the crest of the energy barrier would lie in the entry valley of the collinear surface. The same was true of the 14 exothermic hydrogen-atom transfer reactions, treated according to the BEBO approximation. It seems, therefore, that though Fig. 8(a) may perhaps be appropriate to the special case of \( M+XR \) to which it was originally applied, it is likely to be qualitatively incorrect for the generality of reactions. If the potential-energy changes in the general case can usefully be approximated by a switch from interactions characteristic of reagents to those characteristic of products, it appears more realistic to locate the switching point for exothermic reactions along the coordinate of approach \( r_1 \) as we did in our earlier study.

Since we find on both the LEPS and BEBO approximations that \( r_2^{0,0} \approx 0 \) (i.e., \( r_2^{0,0} \approx r_0 \)) for exothermic reactions, we represent the increased energy of the activated state relative to that of the reagents as arising solely from repulsive interaction between \( A \) and \( B \) \( [E_{\text{A,B}}(r_1)] \). (This is the term that was neglected in the OEP description of \( M+XR \).) Since, however, both \( r_1 \) and \( r_2 \) must alter beyond the activated state, we make the simplest possible division of the energy of the activated state with respect to the products; it is ascribed in part to the potential energy of attraction between \( A \) and \( B \) operating along \( r_1 \) \( [E_{\text{A,B}}(r_1)] \) and in part to repulsion between \( B \) and \( C \) along \( r_2 \) \( [E_{\text{B,C}}(r_2)] \). The degeneracy in the activated state then requires that

\[
E_{\text{A,B}}(r_1) = E_{\text{A-B}}(r_1) + E_{\text{B-C}}(r_2) - q_e. \tag{10}
\]
Energy on the left-hand side is expressed relative to the reagents, terms in on the right-hand side relative to the products. For a more exothermic reaction Eq. (10) still applies, and proved that the functional forms of the terms in remain unaltered, the energy of the degenerate point will fall with respect to the reagents and will rise with respect to the products, as shown in Fig. 8(b). This, in the crudest terms, may describe the origin of the OP relationship. The relationship should, however, be recognized as being in the first place empirical.

It is evident from Fig. 8(b) that a fall in the barrier height for forward reaction, due to a bodily displacement of the product curves with respect to the reagent curves, now causes a shift in the barrier to a larger $r_1$ as required by Eq. (1a). The same barrier-location correlation would apply if the lowering of the barrier were due to a change in the functional form of the terms on the right-hand side of (10); it is impossible for the intersection of the reagent and the product curves to occur at a lower $E_c$ without at the same time being displaced to larger $r_1$. This helps to explain why the present correlations are stronger ones than the OP correlation.

The correlation would not survive, however, if the functional form of the term on the left-hand side of (10) altered. If, for example, $E_{A-B}(r_1)$ became less steep from one reaction to the next, then the activated configuration could occur at a lower energy and at the same time be displaced to smaller $r_1$. Breakdown of the barrier-location correlations due to this cause appears to be somewhat less likely than breakdown of the OP relation due to variation in the functional form of the terms on the right-hand side of the equation, since for exothermic reactions $E_{A-B}(r_1)$ is required to remain constant over a smaller range of $r$ for the present correlation than are $E_{A-B}(r_1)$ and $E_{B-C}(r_2)$ for the OP correlation.

It should be observed that marked variation in the form of $E_{A-B}(r_1)$ is not the only possible cause of failure of the barrier-location (and OP) correlations. Implicit in the discussion in terms of Fig. 8 is the assumption that changes in barrier height can be traced to a shifting balance of forces along a single favored reaction coordinate. To a lesser extent the same assumption enters into the BEBO approximation, which incorporates the requirement of exclusively collinear reaction. However, the BEBO approximation provides for a variety of minimum paths across the collinear potential-energy surface, and hence a variety of reaction coordinates. The extended LEPS equation introduces still greater flexibility. Though the LEPS barrier heights in the present work were taken from the collinear surface, the minimum path across that surface was free to vary. Moreover, the favored angle of approach could deviate from the collinear, in which case we would be measuring too great a barrier height on the collinear surface. There is evidence that for related families of reactions the correlations embodied in Eqs. (1a), (2a), and (3) survive nonetheless.

The approximation of an invariant reaction coordinate, from member to member of a homologous series, will be best for the most exothermic (or most endothermic) members of the series since these have the barrier located well into the entry (or exit) valley of the energy surface, where the reaction coordinate cannot deviate greatly from $r_1$ (or $r_2$). For these reactions it is of interest to analyze Fig. 8(b) in more detail. We can identify the attractive energy release with the first term on the right-hand side of (10) and the
repulsive energy release with the second term on the right-hand side. Inspection of the figure shows that
\[ \Delta \Theta \sim \Delta q - | \Delta E_C |. \]
(11)
Table I tests Eq. (11) for all pairs of reactions with \((\Theta > 0\% \) (this proviso ensures that the barrier is in the entrance valley). The equality is approximately obeyed.

It should be noted that whereas the OEP representation of Fig. 8(a) (assuming unchanged functional forms for the various interactions) demands that the product curve be displaced downwards with respect to the reagent curve, the redrawn picture of Fig. 8(b) by introducing two product curves leaves some choice in interpretation. The greater exothermicity may be represented by either or both an increase of \(E_{k_B}(R_k)\) or of \(E_{k_C}(R_k)\). If only \(E_{k_C}(R_k)\) were increased then the additional reaction energy would contribute exclusively to the repulsive energy release \(\Theta_A; \Theta_A = \Theta_{k_B} + \Delta q_R\) [see Fig. 8(b)]. There would be a decrease in the percentage attractive energy release (\(\Theta_A\)) on going to the more exothermic reaction. This is qualitatively at variance with the findings on the LEPS and BEBO approximations (see Figs. 2, 5, and 6). Table I shows that Fig. 8(b) as drawn, with the entire increase in energy of reaction ascribed to the coordinate of approach, conforms most closely to the predictions from the LEPS and BEBO approximations.

The correlation between barrier location and barrier height [governed by the constant \(\beta_i\) in Eq. (1a)] implies a certain angle \(\Theta_{A_B}\) between the A-B curve and the horizontal in Fig. 8(b). The linear dependence of \(\Delta E_C\) on \(\Delta R_{1,0}^s\) is governed by \(\beta_i\). There is reason to believe that the LEPS equations for families (iii) and (iv) and the BEBO equations for families (i) and (ii) are in each case a fair approximation to reality. The values of \(\beta_i\) for these four families were \(\beta_i = 3, 5, 6, \) and 6. If we take a median figure of \(\beta_i = 5.0\), we can calculate a rough value of \(\Theta_{A_B}\) from the geometric relation
\[ \Theta_{A_B} = \tan^{-1} \beta_i. \]
(12)
The value obtained is \(\Theta_{A_B} = 79^\circ\). This corresponds to a slope of \(\sim 5\) kcal mole\(^{-1}\)/\(A\) for the repulsion between nonbonded A-B at \(\sim 1\) \(A\) (\(\pm 0.5\) \(A\)) beyond the equilibrium separation of the bound molecule.

For two of these families [BEBO (i) and (ii)] the OP relation holds. The value of \(\alpha\) in Eq. (5) is 0.22 and 0.11. Apparently \(\alpha = \beta_i^{-1}\). Since the value of \(\alpha\) depends on both \(\Theta_{A_B}\) and \(\Theta_{A_B}\) (the latter being the angle between the A-B attraction and the horizontal), through
\[ \alpha = [1 + (\tan \Theta_{A_B} / \tan \Theta_{A_B})]^{-1}, \]
(13)
we can calculate for \(\Theta_{A_B} \sim 87^\circ\), corresponding to \(\sim 20\) kcal mole\(^{-1}\)/\(A\). The (hypothetical) angle of intersection of the repulsive and attractive curves at the activated state is then the sum of these two angles, i.e., \(166^\circ\).

The value of \(\gamma_1\) (\(\sim 1\)), governing the relation between \(\Delta (\Theta_A)\) and \(\Delta R_{1,0}^s\) [Eq. (2a)] for the four examples for which \(\beta_i\) was cited above, were \(\gamma_1 = 32, 169, 127, \) and 43. Taking a median \(\gamma_1\) approximately equal to 90, we conclude from these examples that \(\beta_i / \gamma_1 \sim 0.1\) kcal mole\(^{-1}\), in the linear relation between \(\Delta E_C\) and \(\Delta (\Theta_A)\) [Eq. (3)]

The relation between \(\Delta R_{1,0}^s\) and \(\Delta R_{2,0}^t\), Eq. (4), can be understood in terms of the schematic potential-energy surfaces of Figs. 9(c) and (d). Equation (4) states that over the limited range of \(R_{1} (\sim 1\) \(A\)) in which we are likely to encounter energy barriers for related families of exothermic reactions, the deviation of the minimum path from the rectilinear path across the surface can be regarded as being logarithmic. A similar relation would apply to the barriers for endo-
thermic reaction; see Fig. 9(d).

The locations of the crests of the energy barriers for a pair of related reactions are indicated on the energy surfaces. Since it would be confusing to include two sets of potential-energy contours on each surface, we have recorded the corresponding energy profiles, in an approximate representation, directly above each energy surface. [Figure 9(a) resembles Fig. 8(b) with the difference that the direction of exothermic reaction has been reversed to conform more closely to the potential-energy surface which is being illustrated, and the approximation of noninteracting reagent and product electronic states has been lifted.] Figure 9(c) shows that with increasing barrier height (I-\(\rightarrow\)II) the crest of the barrier has moved in a major fashion towards smaller \(R_{1,0}^t\), and to a lesser extent toward larger \(R_{2,0}^t\) [cf. Eqs. (1a) and (1b)]. Both of these changes, and the accompanying decrease in \(\Theta_A\) illustrated in Fig. 9(a), are attributable to a shift in the crest of the barrier to a later position along the reaction coordinate. Though the energy profile shows the increasing barrier height (I-\(\rightarrow\)II) correlating with decreased exothermicity (\(q_1 > q_2\)), in qualitative accord with the OP relationship, this, as has been demonstrated above for both the LEPS and BEBO approximations, is not a prerequisite for the validity of the central correlation, which is the shift in the barrier to a later position along the reaction coordinate, with increasing barrier height for exothermic reaction.

Since the barrier height for the endothermic reaction is given by \(q_1 + E_C\), we have assumed the qualitative applicability of the OP relation in order to be able to predict the direction of shift of the barrier \(E_C^t\) for the endothermic reaction. On this assumption, embodied in the energy profile for the endothermic reaction [Fig. 9(b)], we obtain the inequality \(E_{II} < E_{II}^t\) (in contrast to \(E_1 < E_1^t\) for the same pair of reactions proceeding in the exothermic direction). It follows, in exact analogy with the case of exothermic reaction, that there is also
a shift in the barrier to a later position along the reaction coordinate, with increasing barrier height for the endothermic reaction.

Since with increasing barrier height the barrier moves continually to later positions along the reaction coordinate (with the proviso for endothermic reactions that the OP relation shall apply qualitatively), it would be advantageous to have expressions that provided for the asymptotic approach of $\Delta r_1^{1.0}$ from large values to zero and the asymptotic increase of $\Delta r_2^{1.0}$ from zero to large values, corresponding to the movement of the barrier crest from the entry valley into the exit valley as barrier height increases in a related series of reactions. Up to this point we have expressed all correlations, with the exception of that between $r_2^{1.0}$ and $r_1^{1.0}$, as linear functions, this being the simplest possible form and also having the merit that it conforms to the approximation of the OP relationship. It would appear, however, to be desirable to recast both the OP relation and the correlations embodied in Eqs. (1a), (2a), (3), and (5) in a logarithmic form, in order to encompass the full range of the variables. The curvature in the BEBO plots of $E$ versus $q_r$, $E$ versus $r_1^{1.0}$, and $E$ versus $r_2^{1.0}$ is evident in Figs. 5(i) and 5(iii). It can also be seen in the LEPS $E_C$ versus $q_r$ plots of Fig. 3. As $q_r$ decreases, the increase in $E_C$ is at first slow ($\Delta E_C= -\alpha \Delta q_r$ with $\alpha<<1$), but as $q_r$ decreases to $q_r<0$ (for endothermic reaction), $q_r$ becomes a part of the barrier height, and $\Delta E_C=-\Delta q_r$. The approximately linear relation $\Delta E_C= -\alpha \Delta q_r$ with $\alpha<<1$, as became apparent in
Secs. II and III, is only applicable so long as the barrier remains well out in the entrance valley, $r_1^{1,0} > 0.5 \text{ Å}$. The same is true of the linear relationship $\Delta \log E_C \approx -\beta \Delta r_1^{1,0}$. The following logarithmic forms retain the approximate linear interdependence of the linked variables for small $E_C$ (and hence large $r_1^{1,0}$):

$$\Delta \log E_C = -\alpha' \Delta q_s, \quad (5.1)$$
$$\Delta \log E_C = -\beta' \Delta r_1^{1,0}. \quad (1.1a)$$

In order to obtain a similar expression to (1.1a) with $r_1^{1,0}$ in place of $r_1^{1,0}$ [i.e., the analogue of relation (1b)] we sought an empirical expression for $r_1^{1,0} = f(u(r_1^{1,0}))$, which was more precise than Eq. (4) and which [unlike (4)] could be applied to related series which included both exothermic and endothermic reactions. The relationship obtained was

$$\log r_1^{1,0} = -a r_1^{1,0} - b + c(r_1^{1,0})^{-1}, \quad (14)$$
$$\Delta \log r_1^{1,0} = -a \Delta r_1^{1,0} + c \Delta [(r_1^{1,0})^{-1}]. \quad (4.1)$$

The relationship is tested in Fig. 10; values of $a$, $b$, and $c$ are listed in Table II. Equation (4.1) leads to

$$\Delta \log E_C = \left(\frac{c \beta}{[\log(C/\rho E_C)]_n[\log(C/\rho E_C)]_n + \frac{1}{\beta} \Delta \log r_1^{1,0}}\right)^{-1}$$

The difference $\Delta$ in (1b.1) refers to a change from reaction I to the related reaction II.

Equation (5.1) has the logical advantage as compared with the OP relationship that it provides for $E_C = 0$ as $q_s \to \infty$, instead of predicting negative barrier heights for very large exothermicities. It has already been noted that the OP relation is not a necessary requirement for the validity of the correlations between

---

**Table II. Values of the constants in the relations:**

<table>
<thead>
<tr>
<th>Approximation</th>
<th>Family</th>
<th>$b$</th>
<th>$C_b$</th>
<th>$C_r$</th>
<th>Exo</th>
<th>Endo</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td></td>
<td></td>
<td>2.75</td>
<td>1.98</td>
<td>2.20</td>
<td>1.10</td>
</tr>
<tr>
<td>(b)</td>
<td></td>
<td></td>
<td>5.47</td>
<td>3.97</td>
<td>3.85</td>
<td>1.55</td>
</tr>
<tr>
<td>(c)</td>
<td></td>
<td></td>
<td>16.07</td>
<td>1.07</td>
<td>1.07</td>
<td>1.05</td>
</tr>
<tr>
<td>(d)</td>
<td></td>
<td></td>
<td>1.07</td>
<td>1.07</td>
<td>1.07</td>
<td>1.05</td>
</tr>
</tbody>
</table>

**Fig. 10.** Log$r_1^{1,0}$ versus $-a r_1^{1,0} - b + c(r_1^{1,0})^{-1}$ for five families of reactions: LEPS (iii) and (iii') labeled L(iii) and L(iii') and BEBO (i), (ii), and (iii) labeled B(i), B(ii), and B(iii).
barrier height and barrier location among exothermic reactions. Similarly, relation (5.1) may be inapplicable even qualitatively [examples are LEPS (iv), BEBO (iv), and (v)], but (1a.1) and (1b.1) can still constitute useful relationships for correlating barrier height with barrier location, in exothermic and thermoneutral reactions. However, if (5.1) fails to apply qualitatively, the relationships (1a.1) and (1b.1) will fail to predict the correct shifts in barrier height from one endothermic member of the series to another endothermic member, since they predict a continual shift of the barrier toward larger $r_{\Delta}$ as the endothermic barrier height increases.

Where (5.1) is applicable there exist further relationships, between Eqs. (5.1) and (1a.1) and between (5.1) and (1b.1):

$$\Delta q_e = \frac{\beta_2}{\alpha_2} \Delta_0,$$

$$\Delta q_e = - \left( \frac{\alpha_1}{\beta_2} + \frac{\alpha_1}{\beta_2} \right) \left[ 1 + \log(C_0/C_1) \right] \Delta q_e = \left( \frac{\alpha_1}{\beta_2} \right) \Delta \log r_{\Delta}. \quad (15a)$$

All the relationships (1a.1), (1b.1), (4.1), (5.1), (15a), (15b) now have the possibility (with the proviso stated) of covering the full range of barrier heights, from exothermic to endothermic reactions in Figs. 3, 5, and 6, with one value of $\alpha$ for each family, and also covering the full range of barrier locations defined by $r_{\Delta}$ and $r_{\Delta}$ with one value of $\beta_1$ and $\beta_1$ per family. The curves shown in Fig. 3 and in Columns 1 and 2 of Figs. 5 and 6 were drawn with the aid of the logarithmic relationships (5.1), (1a.1), and (1b.1). The values of the constants, which are least-squares values for the corresponding straight-line logarithmic plots, are given in Table II.

Equation (15a) requires that as the energy of reaction decreases from $>0$ for exothermic reactions to $<0$ for endothermic reactions the crest of the barrier shall move in an approximately linear fashion towards smaller extensions of the new bond. This is illustrated in Fig. 11 for LEPS families (iii) and (iii') and BEBO families (i), (ii), and (iii), all of which obey Eq. (5.1).

Depending on the choice of $\beta_1$ and $\beta_1$, the barrier location for the thermoneutral member of a related series can be made more or less symmetric. Where thermoneutrality arises from the existence of a chemical symmetry ABA in the activated state [as in the thermoneutral member of (iii), Sec. II, or families (iii), (iv), and (v) of Sec. III], $r_{\Delta}$ is to be expected. According to the BEBO approximation the same holds true for accidental thermoneutrality in any H-atom transfer reaction [e.g., H+HCl, family (i), Sec. III]. There is no evidence that $r_{\Delta}$ for all thermoneutral reactions A+BC. There is, however, considerable evidence, set out above, that $r_{\Delta}$ for substantially exothermic reactions and, conversely, $r_{\Delta}$ for substantially endothermic reactions. Equations (15a) and (15b) embody this generalization.

In terms of Fig. 9, these equations require that with decreasing exothermicity and increasing barrier height the barrier moves to the left along the entry valley of the exothermic surface [Fig. 9(a)] and at some later point with increasing endothermicity it is found moving to the right along the exit valley of the endothermic surface [Fig. 9(b)].

We have insufficient evidence to improve upon the roughly linear dependence of $(\Delta \varepsilon_{\Delta})$ on $r_{\Delta}$ for related exothermic reactions, illustrated in Fig. 2 for the LEPS approximation and as obtained also (but not illustrated) for the BEBO approximation. However, when this linear relationship is combined with the logarithmic relationship of Eq. (1a.1) to obtain the interrelation between $E_C$ and $(\Delta \varepsilon_{\Delta})$, the result is obtained for related exothermic reactions,

$$\Delta \log E_C = - (\beta_1/\gamma_1) \Delta (\Delta \varepsilon_{\Delta}). \quad (3.1)$$

This expression was used in drawing the curves in the far right-hand column of Figs. 5 and 6. The values of $\beta_1/\gamma_1$ are listed, along with the other constants, in Table II.
As noted in the context of the linear relationships given previously, the constants whose absolute magnitudes are of interest are those for LEPS families (iii) and (iv) and BEBO families (i) and (ii). Typical order-of-magnitude values based on these examples are \( a \approx 10^{-2} \), \( b \approx 1 \), \( c \approx 1 \), \( d \approx 10^{1} \), \( e \approx 10^{2} \), \( f \approx 1 \), and \( \approx 10^{-3} \) [in units of (kilocalories molar\(^{-1}\))\(^{-1}\) for \( a \), \( b \), \( c \), \( d \), \( e \), \( f \), and \( g \), angstroms\(^{-1}\) for \( b \), \( c \), \( d \), \( e \), \( f \), and \( g \), angstroms for \( c \)].

It will be indicated that \( \alpha \) for endothermic reaction is indicated in Fig. 9(b). This quantity is (in the simplest case; cf. Ref. 18) the energy rise in going from \( r_2 \) to the crest of the barrier for the endothermic reaction. The quantity \( \alpha \) for endothermic reaction is the fraction of the energy required to mount the barrier (i.e., the fraction of \( E_{\text{c}}' = q_{e} + E_{\text{c}} \)) that is taken up in the course of extending the old bond. More briefly, it is the fraction of the endothermic barrier that lies along \( r_2 \). In the exothermic direction \( \alpha \) gives a measure of the extent of vibrational excitation in the new molecule. In the endothermic direction it should be related to the gain in reactive cross section resulting from vibrational excitation of the molecule under attack.\(^{1}\) [In both the exothermic and endothermic directions the role of \( \alpha \) is most clear cut for reactions involving light attacking atoms, especially \( \mathcal{L}+3\mathcal{C} \),\(^{25}\) where the reaction coordinate approximates the rectilinear path implied by Figs. 9(a) and (b).\(^{4}\) It should be instructive in the study of related endothermic reactions to calculate changes in \( \alpha \) by applying Eq. (3.1) to the reverse (exothermic) reactions.

There is rather little experimental evidence at the present time against which to test the correlations obtained in this study. The decrease in barrier height in going from the reaction \( \text{H}+\text{Cl} \rightarrow \text{HCl}+\text{Cl} \) \( (E_\text{d} = 2.0 \pm 0.5 \text{ kcal molar}^{-1}) \) to \( \text{H}+\text{Br} \rightarrow \text{HBr}+\text{Br} \) \( (E_\text{d} = 1.2 \pm 0.5 \text{ kcal molar}^{-1}) \)^{14b,26} correlates with increase in the attractive energy release; \( \alpha \approx 25\% \pm 5\% \) in the former case and \( 35\% \pm 5\% \) in the latter.\(^{21}\) This is in qualitative accord with Eq. (3.1), and is in quantitative agreement if \( b^1/\gamma \approx 2.10^{-2} \), a reasonable figure (see above).

There is some evidence that hydroxyl radicals formed in the reaction \( \text{H}+\text{O}_2 \rightarrow \text{OH}+\text{O}_2 \)^{25} contain a significantly greater fraction of the total reaction energy in vibration than do hydroxyl radicals formed in the reaction \( \text{H}+\text{NO}_2 \rightarrow \text{OH}+\text{NO}_2 \)^{25,26} This would imply, particularly for this \( \mathcal{L}+3\mathcal{C} \) mass combination, that there is a greater percentage attractive energy release in the \( \text{H}+\text{O}_2 \) reaction than in the \( \text{H}+\text{NO}_2 \) reaction. If we can regard these as members of a homologous series (which is somewhat doubtful since \( \text{O}_2 \) is diamagnetic and \( \text{NO}_2 \) paramagnetic), then the decrease in \( \alpha \) in going from \( \text{H}+\text{O} \rightarrow \text{H}+\text{NO} \) may be linked through Eq. (3.1) to increase in \( E_\text{c} \) consequent on a decrease in \( q_{e} \) (both barrier heights, in this case, being \( \leq 1.5 \text{ kcal mole}^{-1} \); the values of \( q_{e} \) are 77 kcal mole\(^{-1}\) for the first reaction and only 30 kcal mole\(^{-1}\) for the second. This example involves more uncertainties than the previous one.

A further link with experiments may be through measurement of angular scattering in crossed-molecular-beam studies. In earlier work\(^{28}\) we have defined a stripping threshold energy \( E_{\text{s}} \), which is a measure of the tendency of a particular reaction \( \text{A}+\text{BC} \) to scatter molecular product \( \text{AB} \) "forward" along the continuation of the direction of approach of atom \( \text{C} \) [viewed in the center-of-mass (c.m.) frame]. The stripping threshold energy \( E_{\text{s}} \) was defined as the c.m. collision energy above which \( >90\% \) of the AB product was scattered into the forward hemisphere. A low stripping threshold energy would be characteristic, therefore, of a reaction for which the forces were conducive to forward scattering. It was suggested that in related series of reactions the value of \( E_{\text{s}} \) would increase with decrease in the magnitude of the repulsive energy release \( \alpha \). This is clearly evidenced in recent classical trajectory calculations.\(^{28}\) It would appear to be a factor of major importance in bringing about the shift toward more-forward scattering with increasing reactive cross section\(^{29}\) \( S \) found in the reactions of alkali-metal atoms with halides.

For the slower of these reactions there are likely to be small activation barriers controlling \( S \). In the present work we have seen the inverse relation between \( E_\text{c} \) and \( \alpha \) applying to related series of reactions with barrier heights of \( \leq kT \) for room temperature. Decrease of barrier height in the region of very low barriers can therefore produce increase in the fraction of the energy release that is attractive (\( \alpha \)) and decrease in the fraction that is repulsive (\( \alpha \)). Provided that \( q_{e} \) does not change markedly this decrease in \( \alpha \) implies a decrease in the absolute magnitude of the repulsive energy release \( \alpha \) and hence an increase in forward scattering, as is observed. An example might be the pair of reactions\(^{26b} \text{Cs}+\text{CHCl}_3 \rightarrow \text{CsCl}+\text{CHCl}_2 \), for which \( q_{e} \approx 36 \text{ kcal mole}^{-1} \), and \( \text{Cs}+\text{CCl}_4 \rightarrow \text{CsCl}+\text{CCl}_3 \), with \( q_{e} = 38 \text{ kcal mole}^{-1} \). The value of \( S \) and the extent of forward scattering are greater for the latter reaction, perhaps indicating decreased \( E_\text{c} \) (as would be expected for the more exothermic reaction in a type-C family) correlating with increased (\( \alpha \)), as required by Eq. (3.1). At the present time it is hard to disentangle this effect from the effect of a possible

25 The symbols \( a \) and \( b \) are used to designate light and heavy atoms, respectively.


change in the extent of "migration" (Cs attracting at first one Cl, then another) and from possible kinematic effects due to reaction at increased impact parameters. It does appear, nonetheless, that this represents a possible future area of application of the correlations described in this paper.

V. CONCLUSIONS

This study, based on the LEPS and BEBO approximations, suggests the following generalizations concerning exchange reactions \( A + BC \rightarrow AB + C \):

1a) Within related series of reactions, increase in barrier height is accompanied by a shift of the barrier to later locations along the reaction coordinate. This generalization applies to both exothermic and endothermic reactions. In the latter case it is contingent on the fact that the reverse reaction shall exhibit decreasing barrier height with increasing reaction energy, in qualitative accord with the Ogg-Polanyi relationship.

1b) In a series of exothermic reactions this correlation can be roughly approximated by the linear expressions \( \Delta E_C = -\beta_1 \Delta r_{1.0} \), with \( \beta_1 \) typically \( \sim 5 \) kcal/mole/Å. A logarithmic form of this relationship, \( \Delta \log E_C = -\beta_1 \Delta r_{1.0} \), is able to embrace not only exothermic but also thermoneutral and endothermic members of a homologous series. A typical value of \( \beta_1 \) is \( \sim 1 \) Å\(^{-1}\). Both the linear and the logarithmic expressions have been shown to apply to families of types C, A, and BC (the letters indicate the atoms being altered from member to member of the family).

1c) These relationships apply even though the Ogg-Polanyi relationship \( \Delta E_C = -\alpha \Delta q_e \) fails.

1d) The shifting of the barrier to later positions along the reaction coordinate implies for a homologous series, including both exothermic and endothermic reactions, that \( \Delta \log r_{1.0} = -\alpha \Delta r_{1.0} + c \Delta r_{1.0} \), with \( \alpha \sim 1 \) Å\(^{-1}\), \( \sim 1 \times 10^{-2} \) Å.

1e) For strongly exothermic reactions \( r_{1.0} \gg r_{1.0} \), i.e., the barrier is well out in the entrance valley of the potential-energy surface, and for strongly endothermic reactions \( r_{1.0} \ll r_{1.0} \), i.e., the barrier is well out in the exit valley of the surface.

1f) In the light of Paper I conclusion 1(e) implies that for strongly exothermic reactions the reactive cross section rises more rapidly with increasing relative translational energy in the reagents than with vibrational energy in the molecule under attack. For strongly endothermic reactions the converse generalization applies; in this case it is vibration that will be of the greatest importance in promoting barrier crossing.

2) The Ogg-Polanyi relationship, linking barrier height to energy release, was tested on several series of thermoneutral and exothermic reactions of types C, A, and BC, and was found to be moderately successful for families of type C, provided that the barriers were well out in the exit valley of the potential-energy surface, i.e., provided the reactions being compared had substantial exothermicity. A logarithmic expression \( \Delta \log E_C = -\beta_1 \Delta q_e \) gave improved agreement with the data for thermoneutral and exothermic reactions. In addition, the logarithmic expression related increasing barrier to decreasing reaction energy from \( q_e > 0 \) (exothermic reaction) down to \( q_e < 0 \) (endothermic reaction). A typical value of \( \alpha \) was \( \sim 1 \times 10^{-2} \) (kcal/mole\(^{-1}\)).

This relation in \( \alpha \), combined with the earlier one [conclusion (1b) above] in \( \beta_1 \), leads to \( \Delta q_e = \langle \beta_1 / \alpha \rangle \Delta r_{1.0} \). It follows that as the energy of reaction decreases from \( q_e > 0 \) for exothermic reactions to \( q_e < 0 \) for endothermic reactions, the crest of the barrier moves in an approximately linear fashion towards smaller extensions of the new bond.

3) In a series of exothermic reactions, as the barrier height decreases the barrier shifts to earlier positions along the reaction coordinate and more of the reaction energy is liberated along the coordinate of approach, i.e., there is an increase in attractive energy release: \( \Delta \log E_C = -\langle \beta_1 / \gamma_1 \rangle \Delta (\alpha_4) \). Typically \( \beta_1 / \gamma_1 \sim 1 \times 10^{-2} \). The effect of increasing \( (\alpha_4) \) in exothermic reactions has been shown previously to be an increase in the fraction of the reaction energy being channelled into vibration in the newly formed bond (this is especially marked for mass combinations \( \pm 3C \)) and increased breadth of the product energy distribution functions. These changes would be expected, therefore, to correlate with decreasing barrier height and, hence, in families of type C, with increasing exothermicity in related series of reactions. Changing mass combination within the family, either in the direction of or away from the \( \pm 3C \) mass combination, could complicate the picture. In homologous series in which the falling barrier is not accompanied by (large) increase in exothermicity, the increase in \( (\alpha_4) \) will be accompanied by a decrease in the absolute magnitude of the repulsive energy release \( \alpha_4 \), with a consequent decrease in the stripping threshold energy \( E_S \).

For endothermic reaction \( \alpha_4 \) gives a measure of the fraction of the endothermic barrier that lies along the exit valley of the potential-energy surface; this is of interest in view of (1f).

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