Theoret. Chim. Acta (Berl.) 67, 439-447 (1985)

THEORETICA CHIMICA ACTA

A simple model for a reaction surface

George G. Hall

Division of Molecular Engineering, Kyoto University, Kyoto 606, Japan

An analytical expression, which has some claim to be the simplest possible, is proposed for the potential governing a collinear reaction. It shows the desired qualitative features but, with only one available parameter, cannot fit a given surface accurately everywhere. The quality of fitting attainable is shown using the surface for the $O+H_2$ reaction.

Because of the simple form of this expression, it is possible to make broad generalizations about such reactions. From a plausible assumption about the parameter value the energy barrier and the transition state geometry can be predicted. These barriers agree well with those suggested by Johnston and Parr for hydrogen transfer reactions.

Key words: Reaction surfaces—hydrogen transfer reactions

1. Introduction

Many attempts have been made to set up formulae to represent a reaction potential. Some have been motivated by theoretical arguments and others by practical considerations. Their principal aim has been to reproduce to high accuracy the potentials obtained from theoretical calculation of the energy at a limited number of nuclear configurations so that the whole surface becomes known by interpolation. Many of these formulae have been reviewed by Wagner et al. [1] and their performance evaluated using a given set of points for the $O+H_2$ reaction. The principal aim of the present work is different. It looks for a form of surface sufficiently simple to be used in later theories without losing the features essential to such a surface.

The potential energy of a diatomic molecule is often represented by the Morse potential

$$V(x)=D(\exp(-2ax)-2\exp(-ax)) \tag{1}$$

where D is the dissociation energy, a depends on the vibration frequency and the distance x is measured from the equilibrium separation, $x = r - r_0$. Although this is not an accurate representation of the potential, it does have the correct qualitative features and is simple enough to have a convenient solution to its Schrödinger equation. It fails to show the true potential when the atoms come very close together i.e. $x = -r_0$ or when they are far apart and subject to the van der Waals attraction. It also fails to represent the potential when the two atoms have a significant electrostatic interaction or when the potential is distorted by an avoided crossing.

The Morse potential consists of two terms. The second term represents the valence attraction between the atoms which depends on the penetration of each nucleus into the outer electron distribution of the other and so decreases exponentially with distance. The strength of the attraction is governed by the value of D. The first term represents the overlap repulsion that sets in when the atoms and their orbitals are pushed too closely together. It becomes effective at a shorter distance than the attraction. The equilibrium at $x = 0$ arises from the balance between these two terms.

The situation envisaged here has three atoms, or three moieties, coming together in a straight line. The potential is to be modelled at the same level of accuracy and sophistication as the Morse potential. Two distances are involved, the two separations between the three atoms. When either distance is large the remaining diatomic potential should reduce to the Morse form. When both distances are reduced the central atom will be bonded to both neighbors but with a smaller attraction because its available valence orbitals must now be shared. The potential needs an extra term to represent this mutual effect.

The problem is made more transparent by applying a mapping to the surface. For the Morse potential the mapping

$$X = \exp(-ax) \tag{2}$$

transforms (1) into

$$V = D(X^2 - 2X). \tag{3}$$

As x becomes large, X becomes small so that the mapping is a kind of inversion and V reduces to zero with X. In this map the potential becomes a simple quadratic function of X. This is the simplest function which shows a minimum.

For the collinear reaction this mapping is generalized to two variables

$$X = \exp(-ax), \qquad Y = \exp(-by) \tag{4}$$

where b and y are defined from the Morse potential for the second distance. The most general quadratic form in two variables is now

$$V = A(X^2 - 2X) + B(Y^2 - 2Y) + 2HXY. \tag{5}$$

This reduces to a Morse potential with dissociation energy A when $Y \to 0$ and to one with energy B when $X \to 0$. The zero of potential is when all three atoms are far apart. Since the values of a, b, A, B are fixed by diatomic information, the only undetermined parameter in V is H. The effect of this final term in V, for $H > 0$, is to reduce the bonding on one side as an atom approaches on the other side so the required mutual effect has been added. This is the model potential which will be discussed here.

2. Features of the surface

The equipotentials of the surface (5) are found by giving V a constant value. For each value of V the result is a conic with a fixed center. The center can be found by eliminating the linear terms. So for its coordinates we obtain

$$(B(H-A)/(H^2-AB), A(H-B)/(H^2-AB)). \tag{6}$$

When the discriminant,

$$H^2-AB, \tag{7}$$

is positive the conic is a hyperbola and, when it is negative, an ellipse. Thus, if H is sufficiently large, V has the typical saddle-point form of a reaction surface. If H is smaller the surface has a stable minimum for the three atom configuration.

The surface can have only one critical point, that at its center. However, because x and y are real, the variables X and Y cannot be negative and the surface has a definite boundary at $X=0$ and $Y=0$. It is possible, then, to have boundary extrema. The point $(1, 0)$ is a minimum on the $Y=0$ boundary and it will also be a minimum in relation to nearby interior points if $H > B$. Similarly $(0, 1)$ will be a local minimum if $H > A$. These two conditions together ensure that the surface is hyperbolic and represents two stable diatomics with a transition point between them. Similarly, if $H < A$ and $H < B$, the surface will be elliptic and will represent a stable triatomic. The boundary extrema are then minimax. If H lies between A and B, e.g. $A > H > B$, the center moves out of the physical region and the nature of the surface changes. For a positive discriminant it remains hyperbolic and it becomes elliptic for a negative one. In either event the surface has one boundary minimum and the bottom of the channel rises steadily therefrom to the minimax on the other boundary. For collinear reactions governed by these linear and quadratic terms in the potential energy there are, therefore, only three types of surfaces, the transition state, the stable triatomic and the stable diatomic. Surfaces showing other features, such as an unstable intermediate, will require higher order terms in the energy to describe them.

The mapping from (x, y) to (X, Y) is continuous but not conformal. This means that topological features, such as the touching of two lines, are preserved but angles are usually changed. In particular, tangents to curves transform into tangents but orthogonal trajectories do not transform into orthogonal trajectories. An unfortunate consequence is that the reaction path in the (x, y) plane, which is an orthogonal trajectory of the equipotentials, does not map into an orthogonal trajectory in the (X, Y) plane.

The gradient of V in the (X, Y) plane has two components

$$V_X = 2(A(X-1)+HY) \qquad V_Y = 2(B(Y-1)+HX). \tag{8}$$

For a horizontal tangent to the potential curve at a point the first must vanish and for a vertical tangent the second. These lines help in understanding the graphs. They intersect at the center which does correspond to the saddle point in the (x, y) plane. The potential energy at the saddle point is

$$V_{\text{col}} = -AB(2H-A-B)/(H^2-AB) \tag{9}$$

and, when the conditions for a saddle point mentioned above are satisfied, this energy is negative and approaches zero only if H becomes very large.

The barrier which the system experiences when it starts from the channel which has y large i.e. $X=1,\ Y=0$ is

$$W = V_{\text{col}} - (-A) = A(H-B)^2/(H^2-AB) \tag{10}$$

while the barrier in the reverse direction is

$$W_R = V_{\text{col}} + B = B(H-A)^2/(H^2-AB). \tag{11}$$

When the discriminant (7) is positive, as it must be for a saddle point, both of these remain positive.

3. The $O+H_2$ potential surface

In order to gain some experience of the model (5) and to discover its practical limitations it has been applied to the triplet surface for the $O+H_2$ reaction. This has been calculated by Whitlock et al. [2] and has been taken by Wagner et al. [1] as a bench mark in their comparisons between fitting functions.

Since this model has only one available parameter, H, it is completely determined by fitting one point. For example, the formula for the barrier height, W, equated to its value gives $H = 134.2$ kcal/mole. Although this choice can be defended thermodynamically, it was considered too biased as a fitting procedure and, instead, an average value of H was taken using the 15 points listed by Wagner et al. as their test sequence. This gives $H = 118$ kcal/mole. The Morse parameters were calculated from data given by Herzberg [3]. The resulting surface is shown, in the (x, y) plane, in Fig. 1 and in the (X, Y) plane in Fig. 2. (In the figures, the energy contours are labelled in kcal/mole.) From the first it can be seen that the traditional shape of a reaction surface is preserved. The channels merge smoothly into one another over the saddle point and oblique cross-sections show the typical Morse profile. A closer inspection shows that the saddle point is lower (7 kcal/mole relative to the $O+H_2$ asymptote) than in the original surface (13.35 kcal/mole). The original potential turns the corner rather more abruptly than the model. This means that the saddle point is at smaller distances (r(OH, HH) = (1.063, 1.096) compared with (1.211, 1.237) given by this model, all distances in Å) but it is still to be found in the OH channel. Because of this

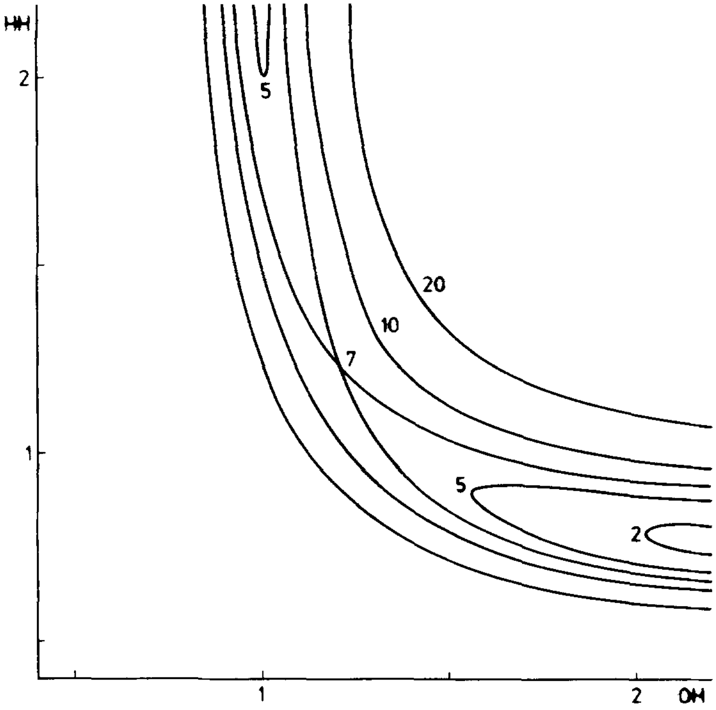

Fig. 1. Potential for the O + H_2 reaction given by the model in Eq. (5) with $H = 118$

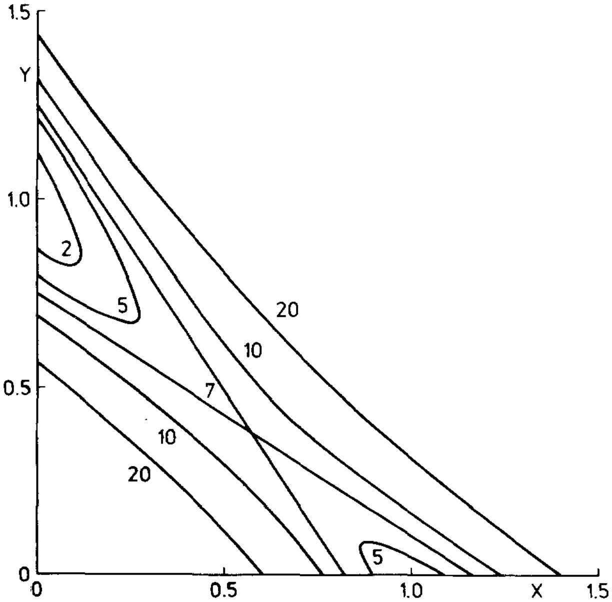

Fig. 2. The potential of Fig. 1 after the exponential transformation

change of shape a point-wise fitting of the surfaces is not very meaningful whereas a comparison along the reaction coordinate shows a much better correspondence.

Fig. 2 shows that the mapping has produced a much simpler surface. The two channels have been aligned and the surface shows symmetry (C_{2v}) about its center. The contour which passes through the saddle point, that for $V = 7$, reduces to a pair of straight lines. These will be features of all the surfaces produced by the model (5) and could have practical value in generating points on the surface.

From the formula for the center given above, it can be seen that the saddle point will lie closer to the OH channel, i.e. to (1, 0), when $B > A$ and closer to the HH channel, (0, 1), when $B < A$. This is the qualitative version of the generalization made by Hammond on the shape of the transition state. The formula for the energy barrier also seems to be in broad agreement with the observations of Evans and Polanyi [4] on barriers for reactions in which only the first atom is varied but has the extra generality of allowing the third to vary also.

4. Barrier energies for H transfer reactions

The surface (5) depends on one parameter, H, to model the coupling between the bonds. If this parameter can be related to the other diatomic parameters, it will become possible to predict surfaces from the diatomic information alone. The example above shows that this cannot be an accurate surface at all points but it can be qualitatively correct and a good approximation in one neighborhood such as around the saddle point itself. Since, in many theories, the reaction rate is determined by this neighborhood, this can be the key to an understanding of the rates of some sufficiently simple reactions in terms of their reactants and products.

The parameter, H, must satisfy several requirements. It should obviously be a symmetrical function of A and B. To retain the saddle point shape it must satisfy $H > A$ and $H > B$ but, generally, it is found best that it should exceed these bounds by the smallest amount consistent with smooth interpolation. Thus, as $B \to 0$, H should tend to A and to B as $A \to 0$. From a cursory inspection of some examples, a plausible value for H, when $A = B$, is $H = 1.2\,A$. A simple formula which meets all these requirements is

$$H = (A^5 - B^5)/(A^4 - B^4) \tag{12}$$

and this is proposed as a working hypothesis. An immediate consequence is a formula for the barrier height

$$W = A^9(A - B)/(A^9 - B^9) \qquad W_R = B^9(A - B)/(A^9 - B^9). \tag{13}$$

When $A = B$ these give $H = 5A/4$ and $W = A/9$. This value of H is a little larger than that suggested above. For the $O + H_2$ potential (12) gives $H = 134.7$ and, hence, $W = 13.97$ which is in good agreement with the original value.

To investigate the realism of this hypothesis the barrier heights have been calculated for the hydrogen transfer reactions studied by Johnston and Parr [5].

The values of the Morse parameters were taken from their paper. They claim that their calculated results are in good agreement with experiment. Since observed activation energies for these reactions involve tunnelling, it was considered better not to compare barrier heights directly with experimental activation energies

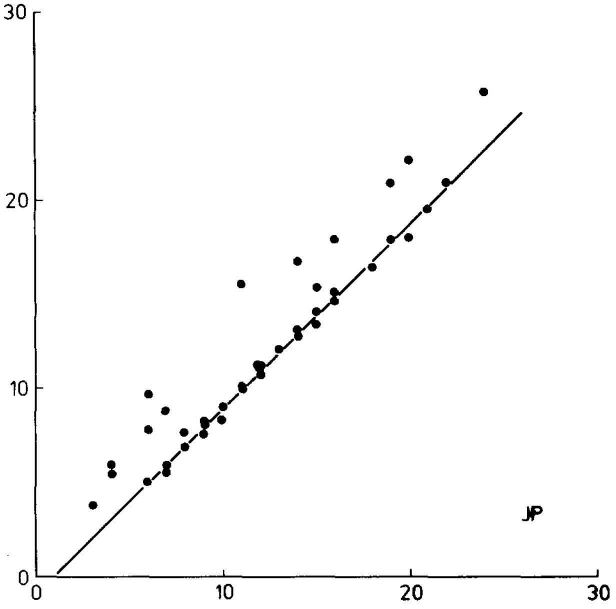

Fig. 3. Reaction barrier heights for non-halogens calculated from equation (13) and compared with those of Johnston and Parr [5]

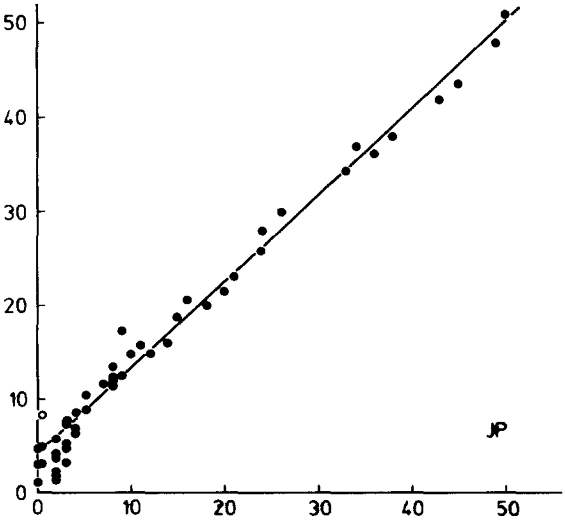

Fig. 4. Reaction barrier heights for systems involving halogens calculated from (13) and compared with those of Johnston and Parr

but with their calculated ones. Fig. 3 shows the barriers calculated by the two treatments for systems not involving halogens and Fig. 4 shows those with halogens. The symmetrical systems, where the atoms on the two sides are the same, have been omitted. These graphs demonstrate a high correlation between the results despite the fact that this is a much simpler calculation than that of Johnston and Parr. In Fig. 3 it can be seen that a majority of the points lie close to a straight line having unit slope but a small negative intercept though some others show a large deviation. In Fig. 4 the points again lie close to a straight line, which has slightly less than unit slope and a small positive intercept, except for a scatter near the origin. For such a simple theory these results are considered satisfactory. The symmetrical systems have been omitted because they have $A = B$ and so are most sensitive to the form taken for H. The fact that the halogens lie on a different line suggests that the large difference in electronegativity between them and hydrogen is giving rise to extra electrostatic terms in the potential.

5. Analytical potentials

The form of the potential in (5) is so simple that it may be regarded as crude and ineffective. This would be a misunderstanding of the significance of the exponential mapping (4). This maps the infinite plane of (x, y) into a finite region of (X, Y) bounded by $X = 0$, $Y = 0$ and the lines corresponding to the internuclear distances becoming zero. In this finite region the polynomials in X and Y form a complete set so that *any* analytical potential can be expressed as a linear combination of powers of X and Y. The model potential V in (5) can be considered as the linear and quadratic terms taken from an exact expression. In principle higher powers can be added to produce any desired accuracy. It is intended to demonstrate this point later. In practice since the interesting region of the plane is the part near the origin the low order powers will be the most important. Higher powers become essential to describe the repulsive region corresponding to small internuclear distances. In any event there is no reason to demand much higher accuracy of the representation of the potential than is achieved by the Morse potentials normally taken to represent the diatomic asymptotic forms. These quadratic forms in X and in Y, in fact, are not very accurate except near the minima when the parameters are determined to achieve a close fit there. The general significance of the Morse potential is that it has the correct qualitative shape and can be taken as a good starting approximation to the true potential. The potential V has a similar significance but its standard of accuracy in relation to the combined variables is lower since only one parameter is available to fit the two-dimensional surface whereas the Morse potential has three parameters to fit along a line.

The Morse potential breaks down when potential curves cross or have an avoided crossing. This will also be true of V. In these circumstances the potential is best regarded as non-analytic and a more general form of V is required.

For a reaction in which the bonds broken and formed are covalent rather than ionic and which has a single potential surface the model potential (5) is the most general form which includes the linear and quadratic powers of X and Y, those which will be the most important in describing the reaction path. The significance of V is, therefore, universal. It is the natural generalization of the Morse potential.

References

1. Wagner, A. F., Schatz, G. C., Bowman, J. M.: J. Chem. Phys. **74**, 4960 (1981)
2. Whitlock, P. A., Muckerman, J. T., Fisher, E. P.: Theoretical Investigations of the Energetics and Dynamics of the Reactions $O+H_2$ and $C+H_2$. Detroit: Wayne State University 1978
3. Herzberg, G.: Spectra of Diatomic Molecules. New York: Van Nostrand 1950
4. Evans, M. G., Polyanyi, J. C.: Trans. Faraday Soc. **34**, 11 (1938)
5. Johnston, H. S., Parr, C.: J. Amer. Chem. Soc. **85**, 2544 (1963)

Received June 13, 1984