

## Marcus Rate Theory and the Relationship between Brønsted Exponents and Energy of Reaction

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**Summary** An intersecting parabola model for the hydrogen atom transfer reaction  $AH + B \rightarrow A + BH$  predicts a linear dependence of the Brønsted exponent  $\alpha$  upon the energy of reaction  $\Delta E$ , consistent with simple Marcus theory, as long as the force constants of the AH and BH bonds are equal and constant and the distance which the hydrogen atom travels is invariant; when these restric-

tions are removed,  $\alpha$  becomes a sigmoid function of  $\Delta E$  whose linear portion, if treated by simple Marcus theory underestimates "intrinsic" barriers by factors of the order of two.

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MARCUS rate theory<sup>1</sup> provides an especially simple relationship between the free energy of activation,  $\Delta G^\ddagger$ , and the

standard free energy change,  $\Delta G^\circ$ , of a chemical reaction; the only other parameter in its basic equation (1) is  $\Delta G_0^\ddagger$ ,

$$\Delta G^\ddagger = \Delta G_0^\ddagger (1 + \Delta G^\circ / 4\Delta G_0^\ddagger)^2 \quad (1)$$

the "intrinsic" barrier or value of  $\Delta G^\ddagger$  when  $\Delta G^\circ$  is zero. This relationship was originally developed for electron transfer reactions, but it has recently been extended to hydrogen transfer,<sup>2</sup> and in this context it promises to provide insight into acid-base catalysis, especially Brønsted relations. For example, it predicts that the Brønsted exponent  $\alpha$ , which may be identified with the derivative  $d\Delta G^\ddagger/d\Delta G^\circ$ , is a simple linear function of  $\Delta G^\circ$ .<sup>3</sup>

To test the validity of Marcus theory, we are comparing its predictions with the behaviour of different models for hydrogen atom transfer. We report the results obtained with a particularly simple analogue, two intersecting parabolic potential energy functions.

The model is shown schematically in Figure 1. It takes the reactant, AH, and the product, BH, of the hydrogen atom transfer process  $AH + B \rightarrow A + BH$  to be simple harmonic oscillators with the potential energy functions  $E_{AH} = k_1 r^2/2$  and  $E_{BH} = \Delta E + k_2(r-d)^2/2$  whose point of intersection represents the activation energy of the reaction,  $E_a$ . Solution of this system of equations gives an explicit function (2) for  $E_a$  in terms of  $\Delta E$  which

$$E_a = \frac{k_1 d^2}{2(1 - k_1/k_2)^2} \left[ 1 - \sqrt{\frac{k_1}{k_2} - \frac{2(1 - k_1/k_2)\Delta E}{k_2 d^2}} \right]^2 \quad (2)$$

contains the two harmonic force constants  $k_1$  and  $k_2$  and the distance between the bottoms of the potential energy wells,  $d$ , as additional parameters.

If  $k_1$ ,  $k_2$ , and  $d$  are constant and  $k_1 = k_2$ , equation 2 reduces to an expression (3, in which  $E_{a,0}$  is the activation energy when  $\Delta E = 0$ ) whose form is identical with equation 1. Marcus has in fact pointed out<sup>2a</sup> that his theory follows

$$E_a = E_{a,0} (1 + \Delta E / 4E_{a,0})^2 \quad (3)$$

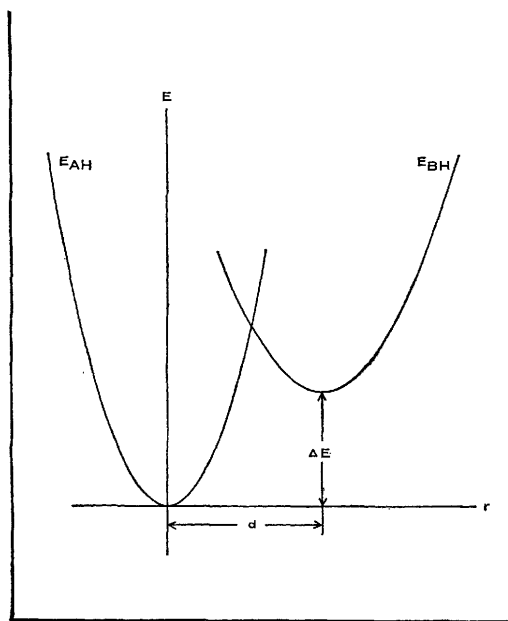


FIGURE 1. Intersecting oscillators model for hydrogen atom transfer,  $AH + B \rightarrow A + BH$ .

from an intersecting parabola model, but he did not state that the two parabolas must have the same constant curvature and a constant horizontal displacement.

It seems unlikely that these two restrictions would be met by real systems. Force constants are a measure of bond strength, and  $k_1$  can therefore be expected to be equal to  $k_2$  only when the strengths of the AH and BH bonds are the same, *i.e.* when  $\Delta E = 0$ ;  $k_1$  will in general be less than  $k_2$  for exothermic reactions and greater than  $k_2$  for endothermic reactions. Similarly, the distance which the hydrogen atom moves,  $d$ , is likely to be greater in the loose activated complexes of strongly exothermic or endothermic reactions than in the tight activated complexes of thermo-neutral reactions; this follows, for example, from the Pauling relationship<sup>4</sup> between bond length and bond order upon which the highly successful BEBO method<sup>5</sup> of predicting reaction barriers is based.

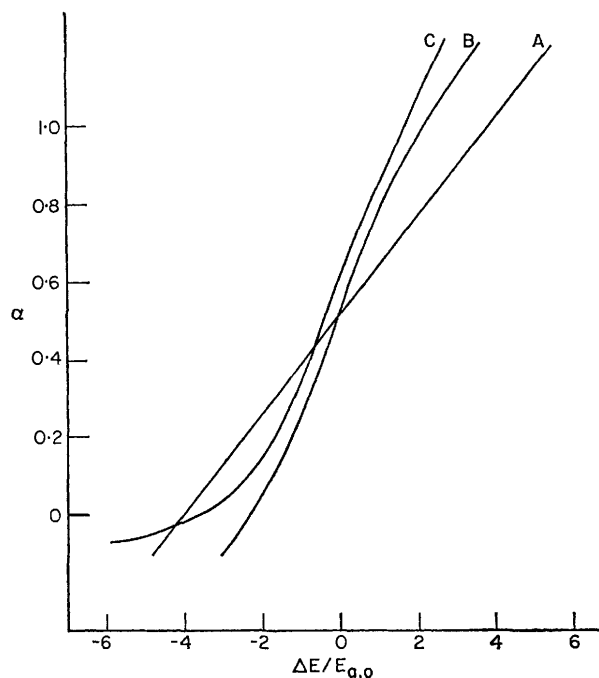


FIGURE 2. Relationship between  $\alpha$  and  $\Delta E$ : curve A, Marcus theory; Curve B, intersecting oscillators with  $E_{AH}$  and  $E_{BH}$  varied; Curve C, intersecting oscillators with  $E_{AH}$  varied and  $E_{BH}$  constant.

To examine the effect of these restrictions upon the intersecting oscillators model, we have evaluated the derivative of equation 2,  $dE_a/d\Delta E (= \alpha)$ , using values of  $k_1$ ,  $k_2$ , and  $d$  which change with  $\Delta E$ . The assignment of  $k_1$  and  $k_2$  was based upon the fact that the X-H stretching force constants of 40 simple hydrides<sup>6</sup> are approximately proportional to their bond dissociation energies,  $D_{XH}$ ; least squares analysis of the data gives a cubic, but nearly linear, relationship between  $k_{XH}$  and  $D_{XH}$  which reproduces the force constants to about 10%. The parameter  $d$  was taken to have a quadratic dependence upon  $\Delta E$ :  $d = d_0 + a(\Delta E)^2$ , both because this is the simplest expression which will give a minimum value at  $\Delta E = 0$  and also because a BEBO model of the same system<sup>7</sup> shows a nearly parabolic relationship between  $\Delta E$  and the distance the hydrogen atom moves. The results of these BEBO calculations were used to guide

selection of the coefficient of  $(\Delta E)^2$ , and  $d_0$  was chosen to give representative values of  $E_{a,0}$ .

This treatment produces a sigmoid dependence of  $\alpha$  upon  $\Delta E/E_{a,0}$  which is rather different from the linear relationship predicted by simple Marcus theory. Curve B of Figure 2 illustrates a typical case for which  $E_{AH} = E_{BH} = 105 \text{ kcal mol}^{-1}$  at  $\Delta E = 0$  and  $E_{a,0} = 10 \text{ kcal mol}^{-1}$ . In this example, both  $E_{AH}$  and  $E_{BH}$  were changed (by equal increments in opposite directions) in order to obtain a variation in  $\Delta E$ , and  $\alpha$  is consequently symmetrically distributed about the point  $\alpha = 0.5$  and  $\Delta E = 0$ . Brønsted relations, however, are usually constructed by changing only one of the reaction partners, the catalyst, while holding the other, the substrate, constant. This relationship, simulated by leaving  $E_{BH}$  invariant at  $105 \text{ kcal mol}^{-1}$ , (Figure 2, Curve C) is now no longer symmetrical and  $\alpha = 0.6$  at  $\Delta E = 0$ . It is interesting in this connection that the hydrolysis of certain vinyl ethers gives Brønsted relations with  $\alpha \simeq 0.6$  when other evidence suggests that  $\Delta E$  ( $\Delta G^\circ$ ) is zero.<sup>8</sup>

Although the present treatment produces an overall dependence of  $\alpha$  upon  $\Delta E$  which is nonlinear, the deviation from linearity in the region  $\alpha$  0.2—0.8, the range of  $\alpha$  normally accessible to experimental determination, is small. The slopes of these nearly linear portions, however, are considerably greater than predicted by simple Marcus theory,  $d\alpha/d\Delta E = 1/8E_{a,0}$ ; for the cases shown in Figure 2, the discrepancy amounts to a factor of two. This has unfortunate consequences upon the growing practice<sup>9</sup> of evaluating intrinsic barriers from the curvature of Brønsted plots. Analysis of the data of Curve B or Curve C according to Marcus theory, for example, would give  $E_{a,0} = 5 \text{ cal mol}^{-1}$ , whereas the value upon which these data are based is  $10 \text{ kcal mol}^{-1}$ .

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