An examination of the BEBO model with the results of ab initio calculations of a reaction series

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An examination of the BEBO model
with the results of ab initio calculations of a reaction series

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Abstract

The BEBO (bond energy–bond order) model of Johnston and Parr is examined with the results of ab initio MO calculations on a series of metathetic reactions which involve hydrogen transfer. Energies are calculated at the 6-31G**/PMP2 = full//6-31G** level while the bond orders are estimated using the 6-31G** basis set with the geometry optimisation at the single configuration unrestricted Hartree–Fock frame. Our analysis reveals that the bond-order exponent in the BEBO theory is greater than unity for the reaction series and the entropy term becomes implicitly present in the BEBO model.

1. Introduction

Johnston and Parr [1,2] laid the foundation stone of the well known bond energy–bond order (BEBO) model according to which the binding energy is taken to be a power function of bond order as

$$E = -Dn^p, \tag{1}$$

where E is the binding energy at the bond order n, D is the bond dissociation energy of the bond in a molecule and p is a constant. This BEBO model has been widely used and extended [3–7] for calculations of energies of activation for many metathetical reactions. The applicability of the BEBO model in metathetical reactions requires that the sum of the bond orders of the bond being formed and the bond being broken should be constant and equal to unity along the reaction path. This postulate of conservation of bond orders along the reaction path was tested earlier by several authors [6,7–10]. Besides, other bonds in the reactant molecules must remain almost passive during reactions.

Various definitions of bond orders have been proposed from time to time. Mayer [11] defined bond orders in terms of the standard density matrix obtained from the ab initio wavefunctions. This definition is now used by workers [12] as a measure of the progress of reactions. Lendvay [10,13] studied the variation of Mayer's bond orders with bond length and found a more consistent trend with bond length than that using chemist's bond order of Pauling [14]. He [10] however, found that conservation of bond orders to unity holds good only approximately during a metathetical reaction, because of the development of small free valence on the migrating atom. In order to establish the non-conservation of Mayer's bond orders during metathesis reactions, we performed several unrestricted Hartree–Fock (UHF) calculations on the reaction

$$\cdot H_1 + H_2 - H_3 \rightarrow H_1 - H_2 + \cdot H_3, \tag{1}$$
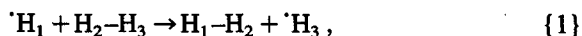
using the several basis sets. Bond orders and free valence on the migrating atom were calculated at the geometric arrangement of the transition state (MEP). Table 1 shows that, for the above reaction {1}, the sum

Table 1
Variation of Mayer's bond orders and free valences on the migrating hydrogen atom during the reaction $H + H_2 \rightarrow H_2 + H$

Basis sets	n_1	$n_1 = n_2$	Free valence
UHF/STO-3G	1.00	0.46	0.08
UHG/3-21G	1.00	0.42	0.15
UHF/4-31G	1.00	0.41	0.16
UHF/6-31G	1.00	0.41	0.16
UHF/6-31G**	1.00	0.44	0.14
UHF/6-311G**	1.00	0.47	0.13
UHF/6-31G**/MP2 = full	0.98	0.47	0.07
RHF/CASSCF(STO-3G)	1.00	0.46	0.08

of Mayer's bond orders of the bond being broken and the bond being formed is not strictly constant and the free valence develops on the migrating atom during reactions. Table 1 also shows results from the standard density matrix obtained at the MP2 level. These results enable us to assert that the non-conservation of Mayer's bond orders during reactions is a real one and not a computational artefact. We cannot therefore use Mayer's definition of bond orders in the BEBO model to find MEP of a reaction. However, we can define the fractional bond orders χ_1 and χ_2 for the bonds being broken and formed, respectively during reactions as

$$\chi_1 = \frac{n_1}{n_1 + n_2},$$

$$\chi_2 = \frac{n_2}{n_1 + n_2}, \qquad (2)$$

where $\chi_1 + \chi_2$ is always equal to unity along the MEP of a metathetical reaction. This definition of χ is also consistent with the classical chemical concept of bond order. We examine the variation of χ calculated via Eq. (2) from ab initio wavefunctions and find that χ follows the similar trend with bond length as expected. It should be pointed out that while n_1 and n_2 are sensitive to the basis sets used for wavefunction calculations, χ_1 and χ_2 are relatively less sensitive.

We therefore rewrite Eq. (1) as

$$E = -D\chi^p, \qquad (3)$$

and by virtue of the principle of conservation of χs, the 'degree (or progress) of reaction' of a metathetic reaction is uniquely determined by, say χ_2, the fractional bond order of the forming bond. One thus obtains for

a metathetic reaction an equation for the minimum energy path as

$$E_{\mathrm{MEP}} = -D_1 \chi_1^p - D_2 \chi_2^q + D_1, \qquad (4)$$

where D_1 is the bond dissociation energy of a breaking bond, and D_2, the bond dissociation energy of a forming bond. The energy is measured from the level of the reactants. Johnston [15] determined the bond-order exponent p for a symmetrical thermoneutral reaction using the observed Arrhenius barrier. In other BEBO calculations the bond-order exponents were estimated from the observed bond energies and the spherically symmetric Lennard-Jones potential energy functions [4,7]. These authors found that the exponents p in Eq. (3) (or Eq. (1)) are close to unity. Eq. (4) was analysed by Marcus [16] where the bond-order exponents p and q were assumed to be unity. Agmon and Levine [17] also used the Eq. (4) with $p = q = 1$ for simple metathetical reactions but added an extra term called the mixing-entropy term. Varandas and Formosinho [18] later used the same BEBO model with $p = q = 1$ including the entropy term and observed that the sum of bond distensions in the transition state depends linearly on ΔE^2, where ΔE is the heat of reaction. Eq. (4) was also used by others [12] in investigations of reaction series where values of p and q were chosen arbitrarily or by non-linear fitting of the data at the extended bond lengths of some simple diatomic molecules [10]. The latter approach could be erroneous as bond orders (χ or n) decrease with increasing bond length much faster in reactive systems than in free molecules. Since the BEBO model plays a significantly important role in physical organic chemistry, we reexamine this model and discuss methods of obtaining the exponents (p, q) in Eq. (4) without any empiricism for a reaction series in which almost similar type of bonds is formed and broken. When a similar type of bonds is broken and formed, p and q can be assumed to be the same. Our investigations are based on the results of ab initio MO calculations for a reaction series in which an almost similar type of bond is formed and broken. Although the ab initio computed results do not represent exactly the observed barriers and heats of reaction, the trends in the ab initio results are significantly similar. The experimental Arrhenius barrier for the reaction $\dot{C}H_3 + CH_4 \rightarrow CH_4 + \dot{C}H_3$ has been reported as 14.7 kcal/M [19], which is less than our computed value. It has been pointed out [20] that the true adiabatic

Table 2
Calculated barriers for some symmetric thermoneutral reactions and bond dissociation energies of the breaking bonds, D_1

Reaction	E_a (kcal/M)	$-D_1$ (kcal/M)	p
$\dot{C}H_3 + CH_4 \rightarrow CH_4 + \dot{C}H_3$	19.2	108	1.28
$\dot{C}_2H_5 + C_2H_6 \rightarrow C_2H_6 + \dot{C}_2H_5$	20.5	105.4	1.30
$(CH_3)_2\dot{C}H + (CH_3)_2CH_2$ $\rightarrow (CH_3)_2CH_2 + (CH_3)_2\dot{C}H$	18.2	103.7	1.28
$(CH_3)_3\dot{C} + (CH_3)_3CH$ $\rightarrow (CH_3)_3CH + (CH_3)_3\dot{C}$	16.4	100.6	1.26

barrier is not directly comparable with the experimental Arrhenius activation barrier and must exceed 18.4 kcal/M for the above reaction. We wish to point out that if p is assumed to be unity for a reaction series, the entropy term is absent in the BEBO model. On the other hand, for $p > 1$, the entropy term becomes implicit in the BEBO model.

2. Theory

We consider a reaction series

$$\dot{R}' + H–R \rightarrow R'–H + \dot{R} , \qquad \{2\}$$

where R', $R = \dot{C}H_3$, $\dot{C}_2H_5$, $(CH_3)_2\dot{C}H$, $(CH_3)_3\dot{C}$.

The reaction series $\{2\}$ includes symmetric thermoneutral, non-symmetric exo- and endo-ergic reactions and the reverse reactions. The actual reactions studied are depicted in Tables 2 and 3. It has been shown earlier [21,22] that the barriers for H abstraction in such reactions is higher for stronger C–H bonds. When primary, secondary and tertiary C–H bonds are broken in the above series, the heights of the barrier

change accordingly. Pross et al. [22] have shown that the singlet–triplet energy gap for the bond being broken is related to bond strength. For the reaction series $\{2\}$ since a nearly similar kind of bond is broken and formed, the exponents p and q are assumed equal to each other. In such a case, the profile for the MEP is given by Eq. (4), where $p = q$. At the top of the barrier, the first derivative of E_{MEP} with respect to, say, $\chi_2^\neq$ is zero. We then have from Eq. (4)

$$\frac{dE_{MEP}}{d\chi_2^\neq} = -D_1 p \chi_1^{\neq\,p-1} \frac{d\chi_1^\neq}{d\chi_2^\neq} - D_2 p \chi_2^{\neq\,p-1} = 0 . \tag{5}$$

Since $\chi_1^\neq + \chi_2^\neq = 1$, we have $d\chi_1^\neq / d\chi_2^\neq = -1$. Eq. (5) may be rewritten as

$$D_1 p (1 - \chi_2^\neq)^{p-1} - D_2 p \chi_2^{\neq\,p-1} = 0 . \tag{6}$$

At this point the second derivative i.e. $d^2 E_{MEP}/d\chi_2^{\neq\,2}$ is given by

$$\frac{d^2 E_{MEP}}{d\chi_2^{\neq\,2}} = -p(p-1)$$
$$\times [D_1(1 - \chi_2^\neq)^{p-2} + D_2 \chi_2^{\neq\,p-2}] . \tag{7}$$

It is negative if $p > 1$, which shows that we have a real maximum at the saddle point. This suggests that the value of the exponent p must be greater than unity. From Eq. (6) one obtains

$$\left(\frac{\chi_2^\neq}{1 - \chi_2^\neq}\right)^{p-1} = \frac{D_1}{D_2} , \tag{8}$$

or

$$\frac{\chi_2^\neq}{1 - \chi_2^\neq} = \left(\frac{D_1}{D_2}\right)^{1/(p-1)} = r . \tag{9}$$

Table 3
Calculated activation barriers, E_a, heat of reactions ΔE, bond dissociation energies D_2 of the forming bond, the transition state bond orders and distensions (Å) for some reactions

Reaction	E_a (kcal/M)	$\chi_2^\neq$	d (Å)	ΔE (kcal/M)	$-D_2$ (kcal/M)
$\dot{C}H_3 + CH_4 \rightarrow CH_4 + \dot{C}H_3$	19.2	0.500	0.548	0.00	108.0
$\dot{C}H_3 + C_2H_6 \rightarrow CH_4 + \dot{C}_2H_5$	16.9	0.518	0.550	-2.97	108.0
$\dot{C}H_3 + (CH_3)_2CH_2 \rightarrow CH_4 + (CH_3)_2\dot{C}H$	14.7	0.532	0.552	-5.49	108.0
$\dot{C}H_3 + (CH_3)_3CH \rightarrow CH_4 + (CH_3)_3\dot{C}$	12.6	0.534	0.554	-7.53	108.0
$\dot{C}_2H_5 + CH_4 \rightarrow C_2H_6 + \dot{C}H_3$	19.9	0.482	0.550	2.97	105.4
$(CH_3)_2\dot{C}H + CH_4 \rightarrow (CH_3)_2CH_2 + \dot{C}H_3$	20.2	0.468	0.552	5.49	103.7
$(CH_3)_3\dot{C} + CH_4 \rightarrow (CH_3)_3CH + \dot{C}H_3$	20.1	0.466	0.554	7.53	100.6

Eq. (9) leads to

$$\chi_2^{\neq} = \frac{r}{1+r},$$

$$\chi_1^{\neq} = \frac{1}{1+r}, \tag{10}$$

where $\chi_1^{\neq}$ and $\chi_2^{\neq}$ are the fractional bond orders at the transition state. If $D_1 = D_2$, $r = 1$, the bond orders at the transition state of a symmetric thermoneutral reaction are given by

$$\chi_1^{\neq} = \chi_2^{\neq} = \tfrac{1}{2}. \tag{11}$$

In a symmetric thermoneutral reaction the saddle point occurs half way from reactant and product, as expected. The energy barrier of a thermoneutral reaction relative to the bond energy D_1 of the reactant follows from Eq. (4) as

$$E_a = D_1(1 - 2\chi_2^{\neq P}) \tag{12}$$

If $p = 1$, $E_a = 0$, Agmon and Levine [7] concluded that there is no thermodynamic driving force in an identity reaction. On the other hand, Koutecký et al. [23] observed that in a symmetric three-center three-electron model for an elementary hydrogen abstraction reaction the collinear approach is exchange allowed with a barrier of about 15 kcal/M. Since all thermoneutral reactions have the observed as well as computed enthalphic barriers, the value of $p = 1$ in Eq. (12) is not acceptable in the BEBO model. If we have $p < 1$, Eq. (12) leads to negative activation barriers for reactions which have positive enthalphic barriers. This means that $p < 1$ should be discarded.

For non-thermoneutral reactions, we define

$$D_1 = D_2 + \Delta E, \tag{13}$$

where ΔE is the exothermicity of a reaction. From Eq. (9), r follows as

$$r = \left(1 + \frac{\Delta E}{D_2}\right)^{1/(p-1)}, \tag{14}$$

$$\frac{dr}{d\,\Delta E} = \frac{1}{p-1}\left(1 + \frac{\Delta E}{D_2}\right)^{(2-p)/(p-1)}\frac{1}{D_2}. \tag{15}$$

The bond orders χ_1 and χ_2 therefore depend on ΔE. We can use the following expression for the transition state bond orders $\chi_1^{\neq}$ and $\chi_2^{\neq}$ as

$$\chi_1^{\neq}(\Delta E) = \chi_1^{\neq}(\Delta E = 0) + \left(\frac{d\chi_1^{\neq}}{d\,\Delta E}\right)_{\Delta E=0}\Delta E$$

$$+ \frac{1}{2}\left(\frac{d^2\chi_1^{\neq}}{d\,\Delta E^2}\right)\Delta E^2 + \dots. \tag{16}$$

A similar expression is valid for $\chi_2^{\neq}$ (ΔE). Using the definition of $\chi_2^{\neq}$ from Eq. (10) we obtain

$$\frac{d\chi_2^{\neq}}{d\,\Delta E} = \left(\frac{1}{1+r} - \frac{r}{(1+r)^2}\right)\frac{dr}{d\,\Delta E}, \tag{17}$$

$$\frac{d}{d\,\Delta E}\left(\frac{d\chi_2^{\neq}}{d\,\Delta E}\right) = \frac{d^2\chi_2^{\neq}}{d\,\Delta E^2} = \frac{d}{dr}\left(\frac{d\chi_2^{\neq}}{d\,\Delta E}\right)\frac{dr}{d\Delta E}$$

$$= \left(\frac{2r}{1+r} - 2\right)\frac{1}{(1+r)^2}\left(\frac{dr}{d\,\Delta E}\right)^2$$

$$+ \left(\frac{1}{1+r} - \frac{1}{(1+r)^2}\right)\frac{d^2r}{d\,\Delta E^2}. \tag{18}$$

From Eqs. (17), (18) and (15) we obtain

$$\left(\frac{d\chi_2^{\neq}}{d\,\Delta E}\right)_{\Delta E=0} = \frac{1}{4D_2(p-1)}, \tag{19}$$

$$\left(\frac{d^2\chi_2^{\neq}}{d\,\Delta E^2}\right)_{\Delta E=0} = -\frac{1}{4(p-1)D_2^2}. \tag{20}$$

Following the expansion (16) for $\chi_1^{\neq}$ and $\chi_2^{\neq}$, we obtain

$$\chi_2^{\neq}(\Delta E) = \frac{1}{2} + \frac{1}{4(p-1)}\frac{\Delta E}{D_2}$$

$$- \frac{1}{8(p-1)}\left(\frac{\Delta E}{D_2}\right)^2 + \dots, \tag{21}$$

$$\chi_1^{\neq}(\Delta E) = \frac{1}{2} - \frac{1}{4(p-1)}\frac{\Delta E}{D_2}$$

$$+ \frac{1}{8(p-1)}\left(\frac{\Delta E}{D_2}\right)^2 + \dots, \tag{22}$$

where the sum $(\chi_1^{\neq} + \chi_2^{\neq})$ is always equal to unity for all values of ΔE along the MEP. Above equations suggest that the location of the barrier, $\chi_2^{\neq}$ is an increasing function of ΔE, the reaction heat, and a decreasing function of D_2, the bond dissociation energy of the forming bond. Stronger the bond being formed, smaller will be the shift of location of the barrier from the saddle point of the identity reaction. Since for the reaction series under consideration $\Delta E/D_2$ is very small (usu-

ally of the order of 10^{-2}), the third and the subsequent terms on the right hand side of Eq. (21) and (22) can be neglected in comparison with the first and second terms. We therefore expect a linear variation of $\chi_2^{\neq}$ (or $\chi_1^{\neq}$) with $\Delta E/D_2$ and the value of p can be estimated from the slopes.

3. Computational methods and results

All calculations were performed using the GAUS-SIAN 92 series of programs [24]. Activation barriers E_a, heat of reactions ΔE, and bond dissociation energies D_1 and D_2 were obtained at the 6-31G**/PMP2 = full//6-31G** level. At the spin-projected MP2 level all other spin contaminants were eliminated. Before spin projection, the $\langle S^2 \rangle$ value ranges between 0.76–0.79 and after annihilation of the spin contaminants the value of $\langle S^2 \rangle$ is 0.75. Transition states for the reactions in the series were always characterised by its having only one negative eigenvalue of the force constant matrix. For all reactions the reaction coordinate near the saddle point was given by the eigenvector corresponding to the imaginary frequency of a vibration and is primarily described by $X = R_1 - R_2$, where R_1 and R_2 are the lengths of bond being broken and formed, respectively during the reaction. This definition of reaction coordinate corresponds to the assymetric stretch of linear tri-atomic molecule and is in agreement with the earlier quantum chemical treatments of reactions which involve exchange of hydrogen [25,26]. The optimised geometries of the transition states for all the reactions reveal that the bonds being formed and broken are almost collinear in the transition state. Bond orders χ_1 and χ_2 were estimated according to Mayer's formulation [11] of bond orders n_1 and n_2 using the first-order SCF density matrix and then via Eq. (2). All these calculations were carried out using the 6-31G** basis set with the complete geometry optimisation in the single configuration unrestricted Hartree–Fock frame for which no bond dissociation problem was met.

Various results of the ab initio calculations for the reaction series {2} are reported in Tables 2 and 3. It should be pointed out that the reverse of the reactions {2} i.e. R'–H + Ṙ → Ṙ' + H–R passes through the same transition state as the forward reaction {2}. Employing Eq. (12) and using the data in Table 2 for symmetric thermoneutral reactions for which $\chi_1^{\neq} = \chi_2^{\neq} = 0.5$, we

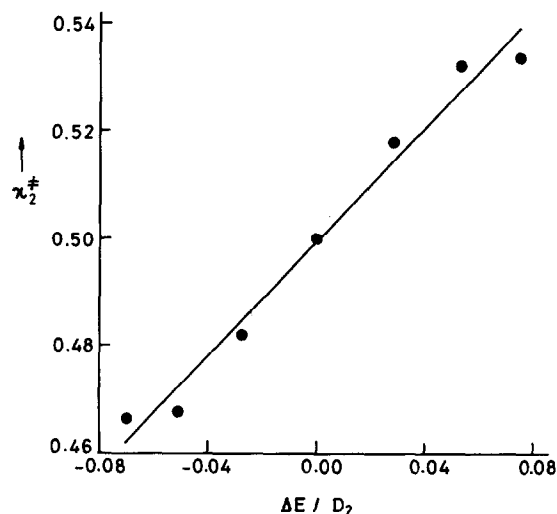Fig. 1. The plot of $\chi_2^{\neq}$ versus $\Delta E/D_2$ for the reactions depicted in Table 3.

obtained the values of p, which are shown in the last column of Table 2. Results reveal that for the reaction series under consideration the value of the exponent p in the BEBO model is greater than unity and is close to 1.3. Using the results of Table 3, $\chi_2^{\neq}$ is plotted against $\Delta E/D_2$ and the least square plot is shown in Fig. 1. From the slope of the nearly linear plot (see Eq. (21)) the value of p was estimated at 1.49. A similar linear plot is observed for $\chi_1^{\neq}$ versus $\Delta E/D_2$ with a negative slope (see Eq. (22)) which also leads to a value of 1.49 for p.

4. Discussion

We have seen that in the BEBO model if the bond-order exponent p is chosen to be unity, there is no thermodynamic driving force for a symmetric ther-moneutral reaction. Agmon and Levine [17] have generalised the BEBO model by including the entropy of mixing term to the potential energy. They have used a parameter λ with dimensions of energy which determines the contribution of the entropy term to the MEP. Agmon and Levine have shown that the bond order $\chi_1^{\neq}$ at the transition state is given by

$$\chi_1^{\neq} = [1 + \exp(\Delta E/\lambda)]^{-1} \qquad (23)$$

From Eq. (10) $\chi_1^{\neq}$ is given by

$$\chi_1^{\neq} = (1+r)^{-1} = \left[1 + \left(\frac{D_1}{D_2}\right)^{1/(p-1)}\right]^{-1}$$

$$= \left[1 + \left(1 + \frac{\Delta E}{D_2}\right)^{1/(p-1)}\right]^{-1}. \qquad (24)$$

Equating Eqs. (23) and (24) we have

$$1 + \exp(\Delta E/\lambda) = 1 + [1 + (\Delta E/D_2)]^{1/(p-1)}$$

or

$$\frac{1}{p-1}\ln\left(1 + \frac{\Delta E}{D_2}\right) = \frac{\Delta E}{\lambda},$$

or

$$\ln\left(1 + \frac{\Delta E}{D_2}\right) = (p-1)\frac{\Delta E}{\lambda}. \qquad (25)$$

Since $\Delta E/D_2 \ll 1$ we have

$$\frac{\Delta E}{D_2} \approx (p-1)\frac{\Delta E}{\lambda},$$

or

$$\lambda \approx (p-1)D_2. \qquad (26)$$

If $p = 1$, $\lambda = 0$, the entropy term is thus absent in the BEBO model. Agmon and Levine [17] were therefore justified in adding the entropy term in the potential energy function. On the other hand if $p > 1$, $\lambda \neq 0$, the entropy term becomes implicitly present in the original BEBO model. Varandas and Formosinho [18] observed that the sum of bond distensions, d, in the transition state for non-thermoneutral reactions has a quadratic dependence on the enthalphy of reaction if the entropy of mixing is added to the BEBO model (with $p = 1$).

We shall now examine the behaviour of the sum of bond distensions, d, in the transition state for non-thermoneutral reactions according to our BEBO model. The sum of bond distensions, d, in the transition state for the reaction series (2) is defined as

$$d = R_{R'-H}^{\neq} - R_{R'-H}^0 + R_{H-R}^{\neq} - R_{H-R}^0, \qquad (27)$$

where $R^{\neq}$ and R^0 are the transition state and equilibrium bond lengths of the bonds indicated as subscripts. The values of d for the various reactions in Table 3 were estimated from the optimised geometries of the transition state structures and the reactants. They are

given in Table 3. The portion of the transition state structures which contain the abstractable hydrogen between the two carbon atoms is always found to be linear for the reactions considered here.

Pauling [14] found a simple relation between the bond order and bond length as

$$-a \ln \chi_{AB} = (R_{AB} - R_{AB}^0), \qquad (28)$$

where R_{AB} is the actual interatomic distance and R_{AB}^0 is the equilibrium bond length, a is sometimes treated as an adjustable parameter [16,27]. Using Eq. (28) we write Eq. (27) as

$$d = -a \ln \chi_2^{\neq} - a \ln \chi_1^{\neq}, \qquad (29)$$

where $\chi_1^{\neq}$ and $\chi_2^{\neq}$ are, as before, the bond-breaking and bond-forming bond orders in the transition state during Reaction (2). We shall now substitute for $\chi_1^{\neq}$ and $\chi_2^{\neq}$, Eqs. (21) and (22) respectively remembering that $\Delta E/D_2$ is small and the third and subsequent terms in the expansions (21) and (22) are neglected. We then have

$$d = -a\left[\ln\left(\frac{1}{2} + \frac{1}{4(p-1)}\frac{\Delta E}{D_2}\right)\right.$$
$$\left. + \ln\left(\frac{1}{2} - \frac{1}{4(p-1)}\frac{\Delta E}{D_2}\right)\right]$$

$$= -a\left\{\ln\left[\frac{1}{2}\left(1 + \frac{\Delta E}{2(p-1)D_2}\right)\right]\right.$$
$$\left. + \ln\left[\frac{1}{2}\left(1 - \frac{\Delta E}{2(p-1)D_2}\right)\right]\right\}$$

$$= -a\left[2\ln\frac{1}{2} + \ln\left(1 + \frac{\Delta E}{2(p-1)D_2}\right)\right.$$
$$\left. + \ln\left(1 - \frac{\Delta E}{2(p-1)D_2}\right)\right]$$

$$= 2a \ln 2 + \frac{a}{4(p-1)^2}\left(\frac{\Delta E}{D_2}\right)^2. \qquad (30)$$

This Eq. (30) is comparable with Eq. (12) of Ref. [18]. Both the equations show a quadratic dependence of d on ΔE^2. In Eq. (12) of Ref. [18] D_2 is implicit in the definition of λ. In Fig. 2 we have shown the least-squares plot of d versus $(\Delta E/D_2)^2$. From the slope and intercept p was estimated at 1.31 and a at 0.395 Å.
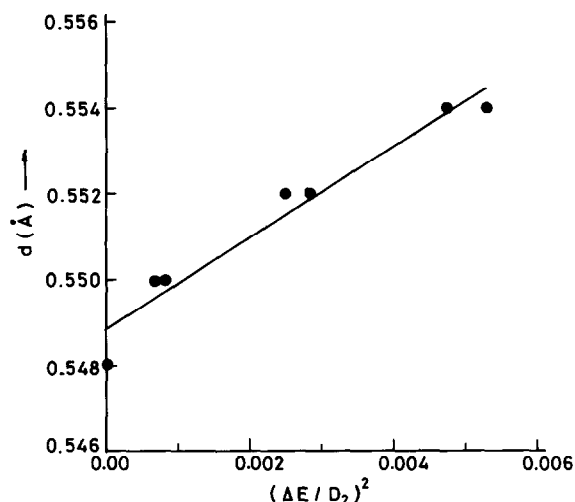
Fig. 2. The plot of distensions, d (Å), in the transition state structures versus $(\Delta E/D_2)^2$ for the same series of reactions.

5. Conclusions

In conclusion, we wish to say that in the BEBO model the bond-order exponent p has a value greater than unity. Although our analysis does not predict a precise value of p, it however shows that the value of p lies in the range of 1.3–1.5 for the reaction series {2}, where a C–H bond is broken and a very similar (but not exactly identical) C–H bond is formed. If the value of p is chosen to be unity in the BEBO model, the potential energy for the minimum energy path does not contain the entropy term. We believe that the BEBO model with $p > 1$ is thermodynamically sound.

Acknowledgement

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