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EXTENSION OF BEBO METHOD FOR THE ESTIMATION OF ACTIVATION ENERGIES OF INTRARADICAL 1,2-HYDROGEN SHIFT REACTIONS

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The bond energy–bond order (BEBO) method of Johnston and Parr for the estimation of intermolecular atom transfer reactions has been generalized for the intraradical 1,2-H atom transfer reactions. The extension includes all the characteristic features of a three-membered cyclic transition state complex. The extended BEBO method has been applied to pentyl-2, ethyl, 1-butene-4-yl and isopropyl radicals isomerization reactions. The agreement between calculated and experimental activation energies is very good. Discrepancies exist in the activation energies of ethyl and 1-butene-4-yl radicals which have large experimental uncertainties, too.

1. Introduction

The intramolecular shift of hydrogen in free radicals has been documented in the liquid and gas phases for transfers involving cyclic transition states larger than five members; i.e. 1,4- and 1,5-hydrogen shifts via five- and six-membered transition states, respectively, have been observed [1]. These studies have been performed using both thermal and chemical activation techniques. Nowadays, isomerization of vibrationally excited hydrocarbon free radicals via intramolecular hydrogen atom migration forms an important class of reactions of alkyl and alkenyl radicals [1,2].

It has long been recognized that 1,2-hydrogen migrations are, too, at least in principle, viable pathways for rearrangement of alkyl radicals [1]. Some years ago, a number of attempts have been made to measure rate constants, activation energies and A factors for these rearrangements to prove that these reactions play an important role in the chemistry of free radicals. The first evidence for the 1,2-hydrogen shift has been given by Tardy [3], Gordon and co-workers [4,5], Ibuki et al. [6] and Szirovicza and Márta [7].

Tardy [3] has shown that the 1,2-hydrogen shift occurs in the n-pentyl radical system

$$CH_3\dot{C}HCH_2CH_2CH_3 \rightarrow CH_3CH_2\dot{C}HCH_2CH_3 \quad (1)$$
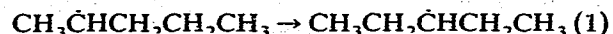
with a critical energy of 33 ± 1 kcal mol^{-1}. In the work of Gordon et al. [4], a mechanism involving isomerization of an ethyl radical by a 1,2-hydrogen (or deuterium) shift along the carbon skeleton competing with abstraction from the parent and decomposition was studied. The kinetics evidenced that the activation energy for
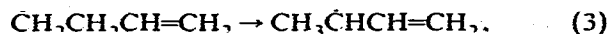
$$CH_3\dot{C}D_2 \rightarrow \dot{C}H_2CD_2H, \quad (2)$$

or

$$\dot{C}H_2CD_3 \rightarrow CH_2D\dot{C}D_2 \quad (2')$$

isomerization of the ethyl radical is 40.7 ± 4 kcal mol^{-1}.

Gordon et al. [5] have proved that the 1-butene-4-yl radical isomerizes to the resonance stabilized butenyl radical

$$\dot{C}H_2CH_2CH=CH_2 \rightarrow CH_3\dot{C}HCH=CH_2, \quad (3)$$

with an activation energy of 20.0 ± 0.7 kcal mol^{-1}. The 1,2-hydrogen shift was substantiated also in the work of Ibuki et al. [6], in which the isomerization of the 1-butene-4-yl radical occurs as given in eq. (3). The threshold energy of the reaction obtained by the RRKM method is 33 kcal mol^{-1}.

The isomerization of the isopropyl radical was investigated in the work of Szirovicza and Márta

[7] by studying the decomposition of azoisopropane. The activation energy of the reaction

$$CH_3\dot{C}HCH_3 \rightarrow CH_3CH_2\dot{C}H_2 \qquad (4)$$
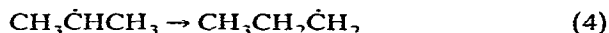
is 36.2 ± 2.1 kcal mol^{-1}.

By geometrical considerations (i.e. strain energy), 1,2- and 1,3-hydrogen shifts should have high energy barriers as compared to 1,4- and 1,5-hydrogen shifts. The small rate constants associated with these high barriers have large experimental uncertainties. Hence, a reliable computational method is desirable to estimate Arrhenius A and E factors of these processes so that a physical model for the hydrogen transfer could be postulated.

The BEBO method of Johnston and Parr [8,9] has been widely used with considerable success to predict activation energies for hydrogen atom abstraction reactions. The non-collinear intramolecular hydrogen atom transfer reactions have not been studied hitherto by this method. We, therefore, have decided to present in this paper the generalized BEBO method for predicting the activation energies of the 1,2-hydrogen intraradical shift reactions.

2. Generalized BEBO method

2.1. The outline of the BEBO method

We repeat briefly the underlying assumptions of the BEBO method. The BEBO method is used to calculate activated-complex properties for hydrogen transfer reactions [8,9]. The calculations are based on a simple linear triatomic valence bond model

$$A-H + B \rightarrow (A...H...B)^{\ddagger} \rightarrow A + B-H, \qquad (5)$$
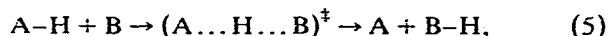
where A and B represent either atoms or groups. The potential energy of the system is calculated along the locus of the line of constant bond order

$$n + m = 1, \qquad (6)$$

where n and m are the bond orders of the A–H bond being broken and the B–H bond being formed, respectively, and where it is assumed that

this is the lowest energy path between the reactant and product. According to this model, the potential energy of the three-atom system A...H...B consists of two contributions: the BEBO-energy contribution of the two bonds of the complex, and the triplet repulsion energy [$V(\text{tripl})$] between the end atoms A and B. The net potential energy $V(n)$ of the system (5) is therefore

$$V(n) = V(\text{BEBO}) + V(\text{tripl}). \qquad (7)$$

Johnston and Parr [8] have given an expression relating bond energy to bond length. When D_n and D_s are the bond energies of the A–H bond of bond order n and a single bond, respectively, then the equation $D_n = D_s n^p$ holds where p is an empirical parameter. Pauling has found a relationship between bond length and bond order [10] which has been further revised by Gilliom [11] into the form

$$r = r_s - 0.28 \ln n, \qquad (8)$$

where r_s is the single bond length in Å. Assuming that noble gas molecules have a bond order equal to zero, the combination of the bond energy–bond order relationship and eq. (8) gives an expression for the parameter

$$p = 0.28 \ln(D_s/D_x)/(r_x - r_s), \qquad (9)$$

where D_x and r_x are the bond strength and length of the noble gas "molecules". Now, the terms in eq. (7) are defined as follows

$$V(\text{BEBO}) = D_{1s}(1 - n^p) - D_{2s}(1 - n)^q, \qquad (10)$$

and

$$V(\text{tripl}) = 0.25D_3\{\exp[-\beta(r - r_3)] + 2\exp[-\beta(r - r_3)]\}, \qquad (11)$$

where p and q are the bond energy indices of the A–H and H–B bonds, respectively; β is the Morse parameter of the A–B bond; D_{1s}, D_{2s} and D_3 are the single bond dissociation energies of the A–H, H–B and A–B bonds, respectively, and r_3 is the single A–B bond length.

The bond order n in eq. (8) is a progress variable changing continuously from 1 to 0 under the condition (6). The maximum value of $V(n)$ for

a certain value of $n = n^{\ddagger}$ gives the potential activation energy $V^{\ddagger}$. The bond lengths of the activated complex, r_1 and r_2, are given in accordance with eq. (8) as

$$r_1 = r_{1s} - 0.28 \ln n,$$
$$r_2 = r_{2s} - 0.28 \ln(1 - n). \qquad (12)$$

In this way a reaction path is defined that starts with reactants, $n(A–H) = 1$ and $n(H–B) = 0$, and ends with products, $n(A–H) = 0$ and $n(H–B) = 1$, that should pass close, if not through the transition state (based upon the success of BEBO). We have thus used n as an intrinsic reaction coordinate and Pauling's relationship as a guide to set forming and breaking bond lengths.

2.2. The BEBO method for the cyclic transition state

For the prediction of the height of activation barriers in intramolecular hydrogen atom transfer reactions we used the model of a cyclic three-atom system described by scheme 1 where H is the transferring hydrogen atom. The potential energy of this complex is a function of the two fractional bond lengths r_1 and r_2 and also of the non-fractionated but little strained bond length r_3. In the case of an intraradical H-atom migration there are, of course, additional effects not present in the one-dimensional collinear transition states. We assume that there are three terms which are mainly responsible for the potential activation energy along the reaction coordinate of the constant bond order in eq. (6) and that these three terms may be treated separately. Thus,

$$V(r_1, r_2, r_3) = V(BEBO) + V(tripl) + V(def). \qquad (13)$$
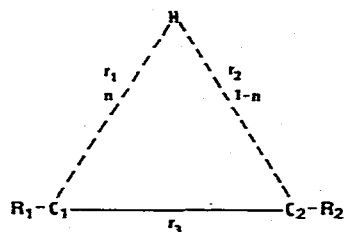
Scheme 1.

where V(def) is the angle deformation energy and the other two terms have already been defined.

2.2.1. The bonding energy term V(BEBO)

According to the BEBO theory [8,9], the bonding energy term V(BEBO) represents the potential energy change for formation of the activated complex (scheme 1) due to the breaking (or formation) of the $C_1 \ldots H$ and $C_2 \ldots H$ fractional bonds, respectively.

Since a conventional hybridization does not permit the description of bond angles less than 90°, we consider the Coulson and Moffitt [12] model of fractional bent or banana bonds as illustrated in fig. 1. Thus, the fractional $C_1 \ldots H$. $C_2 \ldots H$ and partly also $C_1–C_2$ bonds cannot be treated as normal valence bonds. i.e. they are directed not at each other but at angles inclined towards the lines connecting the centers of the carbon–hydrogen and carbon–carbon atoms. Such fractional bonds are strained and the description of this strain must be taken into account in our proposed model of the transition state. Since the bonding energy between two atoms depends upon the overlap integral [13], assuming a simple relation for the bond dissociation energy $D \approx S$, where S is the bond overlap, permits the calculation of the energy of strained bonds.

The hydrogen bonding orbital is a 1s-type orbital and the carbon bonding orbital is largely a 2p-type orbital. Therefore, the bonding energy of the fractional $C_1 \ldots H$ and $C_2 \ldots H$ bonds, respectively, should be approximately proportional to
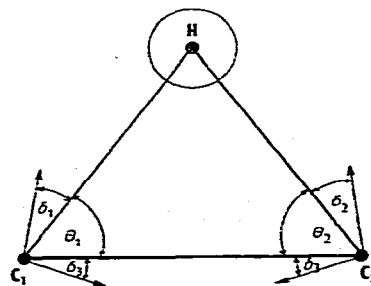
Fig. 1. Model of the activated complex. C_1 and C_2 are the two rigid groups and H is the migrating hydrogen atom: n and $1-n$ are the bond orders. θ_1, θ_2, δ_1, δ_2 and δ_3 are the angles in the "reaction center coordinates".

$\cos \delta_i$, where $\delta_i (i = 1,2)$ is the deviation angle showing the amount of deviation of hybrid orbital directions from the geometric line joining the corresponding nuclei (fig. 1). Thus

$$V(r_1) + V(r_2) = D_{1s}(1 - n^p \cos \delta_1)$$
$$- D_{2s}(1 - n)^q \cos \delta_2. \quad (14)$$

The C_1-C_2 bond, participating in the formation of the three-membered ring transition state complex is also little strained and bent under the assumption that its bond length does not change. We resolve the overlap integral between hybrid atomic orbitals centered at the C_1 and C_2 carbon atoms into σ and π contributions:

$$S(12) = S(\sigma\sigma) \cos^2 \delta_3 + S(\pi\pi) \sin^2 \delta_3. \quad (15)$$

The deviation angle δ_3 from the C_1-C_2 bond is relatively small and is the main factor determining the C_1-C_2 bond strain. Then, once more assuming $V(r_3) \approx S(12)$, permits the estimation of the potential energy strained C_1-C_2 bond

$$V(r_3) = D_3 - D_3 \cos^2 \delta_3 = D_3 \sin^2 \delta_3. \quad (16)$$

Thus, the net bonding BEBO potential energy of the complex (scheme 1), $V(\text{BEBO})$, along the line of constant bond order [eq. (6)], is given using eq. (14) by:

$$V(\text{BEBO}) = D_{1s}(1 - n^p \cos \delta_1)$$
$$- D_{2s}(1 - n)^q \cos \delta_2 + D_3 \sin^2 \delta_3. \quad (17)$$

The BEBO bonding energy eq. (17) for a cyclic transition state is without loss of generality identical to the expression for a simple linear triatomic valence bond model [eq. (10)] as long as we do not take into account the concept of bond strain.

2.2.2. Triplet interaction energy

One crucial point in the BEBO method is the estimation of the triplet repulsion term $V(\text{tripl})$. The quantity $V(\text{tripl})$ represents the repulsive energy of the complex due to the necessary occurrence of parallel electron spins on C_1 and C_2 during the transfer reaction. Suppose the electron on the atom C_1 has spin function $\alpha(\uparrow)$ and forms a fractional bond with the hydrogen atom, which then must have spin function $\beta(\downarrow)$. The central

electron also forms a fractional bond with the electron on the C_2 atom, which then must have spin function $\alpha(\uparrow)$. Thus the relative spin functions of the electrons are:
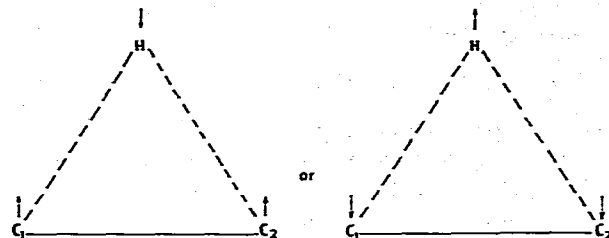
In both cases, the electrons on bonded C_1 and C_2 atoms have parallel spins and repel each other with a triplet interaction. In the limit of negligible overlap [14], the simplified expression for the exchange integral $J(12)$ between two parallel spins is

$$J(12) = \langle \chi_1(\mu)\chi_2(\nu) | e^2/r_{\mu r} | \chi_2(\mu)\chi_1(\nu) \rangle. \quad (18)$$

where $\chi_i (i = 1, 2)$ are two bonding orbitals centered on atoms C_1 and C_2, respectively.

For linear transition states the evaluation of Sato's function [15] is straightforward, since then only σ-type exchange integrals are present [eq. (11)]. In the case of non-collinear transition states, however, it is usually not possible to arrange the atomic orbitals in such a fashion that only σ-type exchange integrals are present. A more general expression must be found which involves the spatial orientations of the selected orbitals as well as the values of the σ- and π-type integrals.

As we have mentioned above, in our transition state model, we work with two non-collinear p-type orbitals χ_1 and χ_2 whose symmetry axes lie in a plane (xz) but are slanted toward each other at angles $\theta_i + \delta_i$ $(i = 1, 2)$ with respect to the internuclear line (the x axis), as illustrated in fig. 1. The atomic orbitals can be resolved as

$$\chi_1 = \chi_1(p_x) \cos(\theta_1 + \delta_1) + \chi_1(p_z) \sin(\theta_1 + \delta_1),$$
$$\chi_2 = \chi_2(p_x) \cos(\theta_2 + \delta_2) + \chi_2(p_z) \sin(\theta_2 + \delta_2). \quad (19)$$

Substitution of these transformations into eq. (18) shows that

$$V(\text{tripl}) = J(p\sigma-p\sigma) \cos(\theta_1 + \delta_1) \cos(\theta_2 + \delta_2)$$
$$+ J(p\pi-p\pi) \sin(\theta_1 + \delta_1) \sin(\theta_2 + \delta_2), \quad (20)$$

where the symbols $J(p\sigma-p\sigma)$ and $J(p\pi-p\pi)$ are used to represent the respective exchange integrals

$J(p\sigma-p\sigma)$

$$= \langle \chi_{1\sigma}(\mu)\chi_{2\sigma}(\nu) | e^2/r_{\mu\nu} | \chi_{2\sigma}(\mu)\chi_{1\sigma}(\nu)\rangle.$$

$J(p\pi-p\pi)$

$$= \langle \chi_{1\pi}(\mu)\chi_{2\pi}(\nu) | e^2/r_{\mu\nu} | \chi_{2\pi}(\mu)\chi_{1\pi}(\nu)\rangle. \quad (21)$$

where $J(p\sigma-p\sigma) \equiv J(p_x\sigma-p_x\sigma)$ and $J(p\pi-p\pi) \equiv J(p_z\pi-p_z\pi)$ resemble diatomic $\sigma\sigma$ and $\pi\pi$ triplet repulsion terms, respectively. By arguing that $J(p\sigma-p\sigma)$ and $J(p\pi-p\pi)$ represent different anti-bonding exchange states, however, they may be represented by Sato's potential [15]

$$J(p\lambda-p\lambda) = 0.25D(p\lambda-p\lambda)$$
$$\times \left\{ [\exp(-\beta_\lambda(r-r_\lambda)+1)]^2 - 1 \right\}. \quad (22)$$

where $\lambda = \sigma$ or π. $D(p\lambda-p\lambda)$ and β_λ are the parameters of the Sato's curve.

Now, with eq. (22) the triplet repulsion energy in eq. (20) can be expressed as:

$$V(\text{tripl}) = V(\text{tripl. } p\sigma-p\sigma) + V(\text{tripl. } p\pi-p\pi). \quad (23)$$

where

$V(\text{tripl. } p\sigma-p\sigma)$
$$= 0.75D_3 \cos(\theta_1+\delta_1)\cos(\theta_2+\delta_2). \quad (24)$$

since $r_3 = r_{3\sigma}$ and $D(p\sigma-p\sigma) \equiv D_3$.

$V(\text{tripl. } p\pi-p\pi)$
$$= 0.25D(\pi)\{2\exp[-\beta_\pi(r_3-r_\pi)]$$
$$+ \exp[-2\beta_\pi(r_3-r_\pi)]\}$$
$$\times \sin(\theta_1+\delta_1)\sin(\theta_2+\delta_2). \quad (25)$$

where $D(p\pi-p\pi) \equiv D(\pi)$ and $r_\pi = r_{3\pi}$ is the bond length of the $C_1=C_2$ π-bond. The arbitrary coefficient in the Sato antibonding function is taken in accordance with Johnston and Parr [8] as 0.25.

2.2.3. Evaluation of the π-bond parameters

In order to evaluate the triplet interaction energy we have to know the values of thermody-

namic and spectroscopic π-bond parameters. At first we mention the π-bond dissociation energy $D(p\pi-p\pi)$. To calculate the π-part of the triplet repulsion energy (20) we must estimate the π-bond dissociation energy $D(\pi)$. Benson and O'Neal [16,17] defined the π-bond dissociation energy in a simple olefin as the difference in the bond dissociation energy of a given bond in the relevant saturated compound and the β free radical. By this definition one gets $D(\pi) = \Delta H_f(\dot{C}-\dot{C}) - \Delta H_f(C=C)$. where $\Delta H_f(\dot{C}-\dot{C})$ is the enthalpy of formation of the hypothetical biradical which has no electronic interactions so that the resonance integral between the carbon atoms and the radical is zero, and $\Delta H_f(C=C)$ is the enthalpy of formation of actual double bond. Thus, the π-bond dissociation energy in for example, 2-pentene is defined as

$$D(\pi CH_3CH=CHCH_2CH_3)$$

$$= DH^0 \left(CH_3 \overset{\overset{\displaystyle H}{\displaystyle |}}{C} HCH_2CH_2CH_3 \right)$$

$$- DH^0 \left(CH_3CH \overset{\overset{\displaystyle H}{\displaystyle |}}{C} HCH_2CH_3 \right). \quad (26)$$

Using the free-radical group additivity scheme of O'Neal and Benson we calculated the bond dissociation energies as given in table 1.

The double bond dissociation energy $D(d)$ is in general defined as the sum of the σ- and π-bond dissociation energy, i.e., $D(d) = D(\sigma) + D(\pi)$. Assuming that a similar expression for the stretching force constants, k, is valid, i.e. $k(d) = k(\sigma) + k(\pi)$, the stretching frequency of the π-bond can be obtained as

$$\bar{\nu}(\pi) = \left(\bar{\nu}^2(d) - \bar{\nu}^2(\sigma) \right)^{1/2}, \quad (27)$$

where $\bar{\nu}(d)$ and $\bar{\nu}(\sigma)$ are the equilibrium vibrational stretching frequency of the double bond, and of the σ-bond respectively. To evaluate the spectroscopic parameter β_π in the Sato potential eq. (22) we use

$$\beta_\pi = 2\pi c\bar{\nu}(\pi)(\mu/2D(\pi))^{1/2}, \quad (28)$$

where c is the speed of light in vacuum, $\bar{\nu}(\pi)$ is

Table 1
Input data used in the EBEBO calculations and parameters of the activated complexes

	Reaction			
	(1)	(2)	(3)	(4)
input data				
D_{1} (kcal mol^{-1}) [a]	41.3	43.0	40.4	43.9
D_{2} (kcal mol^{-1}) [a]	41.3	43.0	43.9	40.4
D_3 (kcal mol^{-1}) [a]	85.3	85.3	85.3	85.3
$D_{=}(\sigma)$ (kcal mol^{-1}) [a]	59.6	61.0	60.3	60.3
$D_{=}(\pi)$ (kcal mol^{-1}) [a]	–	–	48.3	–
k_1 (kcal rad^{-2}) [b]	94.35	92.77	94.35	92.77
k_2 (kcal rad^{-2}) [b]	94.35	92.77	92.77	94.35
output data				
E_a (calc) (kcal mol^{-1})	34.8	35.7	28.2	36.9
V(tripl) (kcal mol^{-1})	26.1	26.7	20.8	26.0
V(BEBO) (kcal mol^{-1})	6.2	6.4	5.4	9.0
V(def) (kcal mol^{-1})	2.5	2.6	2.0	1.9
$n^{\ddagger}$	0.50	0.50	0.55	0.45
δ_1(deg)	31.93	31.49	34.30	30.82
δ_2(deg)	31.93	31.49	30.99	34.30
δ_3(deg)	5.76	5.78	6.75	6.92
E_a(exp) (kcal mol^{-1})	33±1 [c]	40.7±4 [d]	33.0 [e]	36.3±2.1 [g]
			20.0±0.7 [f]	

[a] From ref. [16].   [b] From ref. [18].   [c] From ref. [3].   [d] From ref. [4].   [e] From ref. [6].   [f] From ref. [5].   [g] From ref. [7].

the equilibrium vibrational frequency of the π-bond given by eq. (27), μ is the reduced mass of the two interacting atoms. The $D^0(p\lambda-p\lambda)$ in eq. (22) is obtained by adding the zero-point energy (ZPE) $0.00143\bar{\nu}(\lambda)$, to $D(p\lambda-p\lambda)$ as

$$D^0(p\lambda-p\lambda)(\text{kcal mol}^{-1})$$
$$= D(p\lambda-p\lambda) + 0.00143\bar{\nu}(\lambda). \qquad (29)$$

where $\bar{\nu}(\lambda)$ is the vibrational frequency of the bond in cm^{-1}.

The Badger rule [19] expresses the relation between force constant k and interatomic distance r. For all the quadratic force constants of the ground and excited states of diatomic molecules consisting of B, C, N and O, k is approximately given by

$$k\ (\text{mdyn Å}^{-1}) = 1.86/(r-0.68)^3, \qquad (30)$$

with r in Å.

In the 3ps butenyl radical isomerization reaction, the effect of conjugation between the transition state and the neighbor π-bond is not negligi-
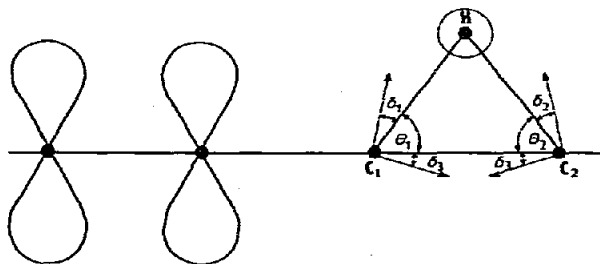

Fig. 2. Interacting model of the transition state with the neighbouring π-bond.

ble. However, since we consider the combined effect of conjugation and repulsion triplet interaction, it is advisable to make the estimation of the conjugation energy as accurate as it is compatible with the BEBO method principles. If we denote the dissociation energy of the isolated π-bond as $D_=(\sigma)$ and the π-bond dissociation energy of the neighbor double bond as $D_=(\pi)$, then for the

dissociation energy $D(\pi)$ of the π-bond in the activated complex we can write

$$D(\pi) = D_\sigma(\pi) + [D_\sigma(\sigma) - D_\sigma(\pi)]$$
$$\times \cos(\theta_1 + \delta_1), \tag{31}$$

where the angles δ_1 and θ_1 are defined in fig. 2 and $D_\sigma(\delta) - D\pi(\pi)$ expresses the conjugation effect of one odd electron over the neighbor atom bearing free valency. Combination of this expression with eq. (25) for the π–π triplet repulsion energy gives the desired total triplet interaction energy of the activated complex.

2.2.4. Transition state deformation potential energy

To illustrate the predicted behavior of the activation energy we must estimate the deformation energy of the valence angle connected with the cyclic transition state formation (fig. 1). To do this, we have chosen the approximated form of Pliva's potential [20]

$$V(\text{def}) = \tfrac{1}{2}k \, \sin(\tfrac{1}{2}\hat{\theta}) \, \sin^2(\theta - \hat{\theta})/\sin(\tfrac{1}{2}\theta). \tag{32}$$

where k is the $H \ldots C_{1(2)}C_{2(1)}$ bending force constant, $\theta - \hat{\theta}$ is the angle deformation coordinate, i.e. the difference between the instantaneous valence angle θ and its equilibrium value $\hat{\theta}$. Pliva's potential is one of the simplest possible functions which adequately reproduces the values of the corresponding cubic and quartic deformation potential constants obtained from experimental data.

The activation of the $C_{1(2)} \ldots H$ bond decreases the equilibrium bending force constant $k(HC_{1(2)}C_{2(1)}) = k_{1(2)}$. Here, the corresponding fractional bond-bending force constant for the bonds involved in the transition state formation are evaluated by the O'Ferrall approximation [21,22]

$$k_1 = k(HC_1C_2)n(C_1 \ldots H)^2,$$

$$k_2 = k(HC_2C_1)n(C_2 \ldots H)^2. \tag{33}$$

Thus, the resulting transition state deformation potential energy contribution $V(\text{def})$, which corresponds to the chosen strained model of the transition state formation and is approximated by Pliva's potential of eq. (32), can be written in the form

(see fig. 1)

$$V(\text{def}) = V_1(\text{def}) + V_2(\text{def})$$
$$= G_1 \sin^2(\theta_1 + \delta_1 + \delta_3 - \hat{\theta}_1)$$
$$\times \left\{ \sin[\tfrac{1}{2}(\theta_1 + \delta_1 + \delta_3)] \right\}^{-1}$$
$$+ G_2 \sin^2(\theta_2 + \delta_2 + \delta_3 - \hat{\theta}_2)$$
$$\times \left\{ \sin[\tfrac{1}{2}(\theta_2 + \delta_2 + \delta_3)] \right\}^{-1}. \tag{34}$$

where

$$G_1 = \tfrac{1}{2}k_1 n(C_1 \ldots H)^2 \sin(\tfrac{1}{2}\hat{\theta}_1).$$

$$G_2 = \tfrac{1}{2}k_2 n(C_2 \ldots H)^2 \sin(\tfrac{1}{2}\hat{\theta}_2). \tag{35}$$

3. Activation energy calculations

The minimum-energy reaction path which is the most probable course of 1,2-hydrogen shift across the surface that allows the least energy for each successive point on the path was calculated on the assumptions formulated through eqs. (17), (23) and (34)

$$V(r_1, r_2, r_3)$$
$$= D_{1s}(1 - n^r \cos \delta_1) - D_{2s}(1 - n)^q \cos \delta_2$$
$$+ D_3 \sin^2 \delta_3 + 0.75D_3 \cos(\theta_1 + \delta_1) \cos(\theta_2 + \delta_2)$$
$$+ 0.25D(\pi) \exp[-\beta_\sigma(r_3 - r_\sigma)]$$
$$\times \left\{ 2 + \exp[-\beta_\sigma(r_3 - r_\sigma)] \right\}$$
$$\times \sin(\theta_1 + \delta_1) \sin(\theta_2 + \delta_2)$$
$$+ G_1 \sin^2(\theta_1 + \delta_1 + \delta_3 - \hat{\theta}_1)$$
$$\times \left\{ \sin[\tfrac{1}{2}(\theta_1 + \delta_1 + \delta_3)] \right\}^{-1}$$
$$+ G_2 \sin^2(\theta_2 + \delta_2 + \delta_3 - \hat{\theta}_2)$$
$$\times \left\{ \sin[\tfrac{1}{2}(\theta_2 + \delta_2 + \delta_3)] \right\}^{-1}. \tag{36}$$

The reaction path is determined by the bond order n (or by the length r_1 of the breaking C_1–H bond) and the energy of the system is maximized with respect to n and minimized with respect to the deviation angles δ_i ($i = 1, 2, 3$). In the calculation procedure, the bond order n is changed step by step from 0 to 1, and for each chosen value of n

the potential energy of the system $V(n)$ is minimized with respect to the variables δ_i. At a certain value of n the value of $V(n)$ attains the maximum $V^{\ddagger}$ corresponding directly to the potential activation energy.

4. Results and discussion

For the H-atom collinear transfer reactions, the BEBO method seems the best a priori method both for computing the barrier height and the barrier position. The theory, as originally formulated, considers a hydrogen transfer between atoms or radicals in their doublet ground states and we have extended it to intraradical 1,2-hydrogen transfers. In this paper we have applied the extended BEBO (EBEBO) method to the hydrogen shifts in the alkyl and alkenyl radicals in their doublet ground state.

The following assumptions were introduced in the EBEBO method: (i) The total bond order around the H-atom is constant and equal to unity not only in the case of collinear transition states but for the cyclic transition states, too. (ii) Pauling's relation eq. (8) holds for the strained fractional bond lengths $C_1 \ldots H$ and $C_2 \ldots H$, involved in the cyclic transition state, too. (iii) The little changes of the C_1-C_2 bond length due to triplet interaction and by the strain were neglected.

BEBO calculations are rather sensitive to the input parameters [23]; therefore, it is necessary to select carefully all bond properties used in them. The calculations in this paper were carried out using the following bond lengths: $r_{1s} = r_{2s} = 1.092$ Å [18], $r_3 = 1.515$ Å [24]. All bond angles were considered to have the standard value of $109.47°$. The β_{π} parameter in Sato's potential from eq. (28) is 2.666 Å^{-1} and the corresponding bond length r_{π} calculated from eq. (30) is 1.356 Å. Further data used in the calculations and calculated and experimental values of the activation energies are shown in table 1. The calculation does not include the change in thermal energy content of the reactants upon activation, and for this reason the activation energies refer to absolute zero. Comparison of the observed and predicted activation energies demands the adjustment of the calculated

and observed values from the experimental temperature to some common temperature which we have chosen to be 298 K. These adjustments are contingent on estimating the heat capacity of the transition states. The corrections are never larger than 2 kcal mol^{-1}, and the error in them was estimated to be less than the expected inaccuracies from other sources. Obviously, the calculated activation energies cannot be more accurate than the molecular data used and care was exercised to obtain the best values available.

The potential activation energies $V^{\ddagger}$ for 1,2-hydrogen shifts are shown in table 1. Strictly speaking, $V^{\ddagger}$ is connected with the experimental activation energy by a complicated equation given in ref. [25]. However, in view of the empiricism involved in the BEBO method the calculated $V^{\ddagger}$ may be directly compared with the experimental activation energy ($V^{\ddagger} = E_a$). Thus the agreement between experimental and calculated activation energies seems to be very good considering the experimental error and the empiricism of the BEBO method. Except for the 1-buten-4-yl radical, the calculated E_a fall within 2 kcal mol^{-1} of the experimental values. The large discrepancy found between calculated and experimental activation energy for this radical published by Ibuki et al. [6] can be explained in terms of the unusually large systematic errors in the rate constants in comparison with the original experimental study of Gordon et al. [5]. This statement is correct of course only if the differences in activation and critical energies are small. However, there are some difficulties in comparing calculated and experimental activation energies [26], because in the case of reactions (1) and (3) only critical energies are available. The potential-energy profile along the reaction coordinate represents the minimum energy path for the reaction, and the critical (or threshold) energy E_0 is the difference between the zero-point energies of the reactant and the activated complex. This critical energy is in general not exactly equal to the experimental activation energy E_a, which is defined quite generally in terms of the slope of the Arrhenius plot. The experimental threshold energy is usually dependent on the detection sensitivity and on the minimum relative translational energy accessible.

Higher discrepancy between the experimental and calculated value (within experimental uncertainties) was also found for the 1,2-hydrogen (or deuterium) shift in the ethyl radical, but even the experimental activation energy exhibits large scattering. The high barriers are associated with a small rate constant and hence, they have large experimental uncertainties. The results may be understood in terms of a mechanism involving isomerization of the ethyl radical (see below).

The general accuracy of the EBEBO method as demonstrated in table 1 guarantees that our results are not fortuitous and that the assumptions and approximations made in its formulation are reasonable. From the agreement between calculated and experimental values we can conclude that the extended BEBO method satisfactorily explains the 1,2-hydrogen transfer reactions. The process can be envisioned by the following way: In the extended BEBO approach, the minimum-energy reaction path involves carbon–hydrogen stretching and bending such that the hydrogen is "exiting" in a direction toward the non-bonded carbon (C_2); the maximum energy on the minimum-energy reaction path corresponds with the hydrogen and the two carbon atoms at the vertices of a triangle. From a static point of view, the hydrogen atom in this configuration has three possible reaction paths: (i) decomposition, (ii) addition to the carbon C_2 producing an isomerized radical, or (iii) remaining on the carbon C_1, producing the original radical. The actual probability of each path depends on the trajectories (motions) involved.

Table 1 shows that the major factor controlling the reactivity in the gas phase intraradical H-transfer reactions is taken into account by the triplet repulsive term. From spin configurations depicted above we see that the contribution of the C_1-C_2 carbon bond to the transition state must correspond to a repulsive triplet state: thus the spin configuration on the C_1-C_2 bond contributes significantly to the potential energy with a repulsive term $V(\text{tripl})$ in eq. (13). A reasonable explanation of this situation can be found in ref. [27]. For a three electron system, the lowering of energy by resonance among the valence-bond structures is very sensitive to the actual geometry of the system. The equilateral geometry is an extreme case (iso-

merization of the ethyl radical) for which there is no resonance energy at all, because the doublets are two orthogonal components of the degenerate symmetry representation. On the contrary, the two doublets for a collinear array do not belong to the same irreducible symmetry group, and can therefore interact, giving rise to a resonance energy. Consequently, the activation energy of a collinear array is lower than the activation energy of an equilateral triangle transition state.

But this repulsive term arises from a pure quantum effect and is in no way related to the spin–spin repulsive energy [28]. Accordingly, in the procedure commonly employed for the treatment of reactions of triplet species, we used Sato's function modified by a factor of 0.25 in order to match the theoretical curve for the π-bond repulsive triplet state at short interatomic distances. The equivalence of the bond character of the rupturing C_1-H and forming C_2-H bond attributes a symmetry to the transition state, i.e. the character of the transition states of all radical isomerization reactions (table 1) is in between that of the less stable and more stable isomers ($n^{\ddagger} \rightarrow 0.5$).

To our knowledge there have been a little number of ab initio calculations reported on the barriers to hydrogen migration in open-shell radical or triplet molecules. One calculation on hydrogen migration in an ethyl radical has been reported [29]. Using the unrestricted STO-3G and 4-31G approximations the barrier for H-atom migration between the carbon atoms was found to be 60.4 kcal mol^{-1}. This calculation is, however, of more qualitative significance than a quantitative value (see table 1) due to the limited size of the basis set and the neglect of electron correlation. Very recently, Harding [30] has reported ab initio POL CI calculations on the barrier to migration in an ethyl radical, too, and the predicted barrier is 46 kcal mol^{-1}. On the basis of his calculations Harding has concluded that in simple alkyl radicals (and triplet carbenes) the lowest energy pathway for 1,2-hydrogen migration will be C–H bond cleavage in most cases followed by reattachment. This conclusion is in good agreement with our results (table 1).

The above EBEBO method by which we estimated the activation energies of the 1,2-hydrogen

shifts, is used in the following articles to investigate the intramolecular 1,3-, 1,4-, etc., hydrogen shift in various radicals and biradicals.

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