Comparison of Theoretical Criteria for the Participation of Tunneling Mechanism in Chemical Reactions

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Comparison of some theoretical criteria of tunneling effect participation in chemical reactions has been carried out. The predictions of characteristic temperatures and tunneling factors are confronted with the experimental data of intermolecular and intramolecular H atom transfer reactions. The calculations have been performed for two different models of tunneling. The results show strong dependence of the theoretical criteria on the accuracy of the estimation of potential barrier dimensions which lowers the reliability of the predictions. The best agreement between the criteria and experimental data has been reached for vibrational-adiabatic barriers. For exo- and endothermic reactions in condensed phase, the criteria obtained in the framework of the tunneling bonding particle model have appeared to be the most convenient. The criteria based on the model of the tunneling free particle are suitable for reactions in gaseous phase and, in special cases, for athermic reactions in condensed phase.

In the study of the kinetics of transfer reactions of electrons, atoms and molecules, mainly in condensed phase at low temperatures, the problem of determination of the tunneling contribution to the total reaction rate often appears. For this purpose, two criteria have been suggested [1—7]. The various modifications of the first one have been proposed by *Goldanskii* [1, 2], *Christov* [3—5], and *Bruhks* and *Jortner* [6]. It consists in the calculation of the so-called characteristic temperature T_c, *i.e.* the temperature below which the tunneling effect plays an important role. *Goldanskii* [1] determined it from the maximum of the function in the integral $\int_0^\infty E\ P(E)\ \exp(-E/RT)\ \mathrm{d}E$ for the parabolic barrier in the form

$$T_c = h(V_0/2\mu)^{1/2}/(2\pi^2 k_B \ell) \qquad (1)$$

where $P(E)$ is the transmission probability, ℓ is the half-width of potential barrier, V_0 is its height, μ is the reduced mass of the tunneling system and the other symbols have their usual meaning.

Christov [3] obtained the formula for T_c from the condition that the averaged probability of passing through the potential barrier by the tunneling mechanism ($E < V_0$) equals that of passing in the classical way over the barrier ($E > V_0$). The resulting form for T_c is

$$T_c = h(V_0/2\mu)^{1/2}/(\pi^2 k_B \ell) \qquad (2)$$

Besides eqn (2), *Christov* [4, 5] has suggested a less exact formula for T_c calculation

$$T_c = h(V_0/6\mu)^{1/2}/(2\pi k_B \ell) \qquad (3)$$

Eqns (*1*—*3*) can be used for any potential barrier having the parabolic curvature in the maximum. In the latter paper *Christov* [5] used T_c for a more detailed classification of tunneling contributions: $T > 2T_c$ tunneling is negligible, $T_c < T < 2T_c$ small, $T_c/2 < T < T_c$ moderate, $T < T_c/2$ large.

The reviewed equations for T_c calculation have been derived using the model of the tunneling free particle (TFP) and could not be used for the model with a discrete spectrum of reactant energies [7], *i.e.* for the model of the tunneling bonding particle (TBP). Usability of T_c calculation according to eqn (*1*) for TBP model was partly discussed by *Goldanskii* [2], but a more solid analysis of the problem has been done even by *Bruhks* and *Jortner* [6]. Studying electron transfer reactions and using the nonradiative nonadiabatic theory of multiphonon processes, the authors obtained the expression for T_c in the form

$$T_c = \hbar\omega(p - q)^2/\{4k_B q[q + \gamma p + 1/2 \ln(2p(q + \gamma p)/(p - q)^2)]\} \qquad (4)$$

where $q = d^2\mu\omega/(2\hbar)$, d is the horizontal distance of potential minima, $p = |\Delta V|/(\hbar\omega)$, $\gamma = \ln(p/q) - 1$, ΔV is the difference of energy between the two minima and ω stands for the frequency of transfer between the two potential wells (or surfaces). Eqn (*4*) was derived under the assumption that the tunneling and classical rates are equal. Further, the equation is applicable only for exoergic systems and under conditions $q \neq p$, $q \neq 0$, $p \neq 0$.

The other criterion for the classification of tunneling contribution has been suggested by *Bell* [7]. His approach is based on the calculation of tunneling factors $\Gamma(T)$, *i.e.* the quantum correction

on the motion along reaction coordinate for temperature T, which may be defined as the ratio of the thermally averaged quantum-mechanical transmission probability $P(E)$ to the thermally averaged classical transmission probability $P_c(E)$

$$\Gamma(T) = \int_0^\infty P(E) \exp(-E/RT)\, dE / \int_0^\infty P_c(E) \exp(-E/RT)\, dE \qquad (5)$$

According to $\Gamma(T)$ values, the tunneling contributions have been divided into the three groups: $1 < \Gamma(T) < 1.1$ tunneling is negligible, $1.1 < \Gamma(T) < 4$ small to moderate, $\Gamma(T) > 4$ large. Use of the tunneling factor as a criterion of the extent of tunneling participation in chemical reactions is less frequent than that of the critical temperature.

One could hardly estimate the usability and reliability of the criteria because there exists no paper comparing the results of both approaches and involving comparison of the calculations with experimental data. For this reason, the present work is devoted to the study of selected H atom transfer reactions. In the case of H + H_2 exchange reactions, the results of T_c and tunneling factor calculations are compared mutually as well as with the experimental data of the rate constant dependence on temperature. The calculations are carried out for various potential barriers within the framework of TFP model. The results of T_c calculations for the TFP and TBP models are compared for the isomerization of 2,4,6-tri-*tert*-butylphenyl radical with the aim of testing the TFP model for systems more convenient to be studied by the TBP one. The predicted T_c values are compared with the corresponding experimental data. Further, we test the dependence of T_c and $\Gamma(T)$ on asymmetry of different potential barriers for the TFP model. This study is carried out for three model reactions of intermolecular H atom transfer (set I). Also, the dependence of T_c on ΔV, d, and ω (eqn (*4*)) is examined for another set of intramolecular H transfer model reactions (set II) as the original work [6] lacks a more detailed discussion.

CALCULATIONS AND RESULTS

Dimension of the Potential Barriers

The dimensions were obtained for individual reaction systems as follows: reaction H + H_2, isomerization of 2,4,6-tri-*tert*-butylphenyl radical and model reaction sets.

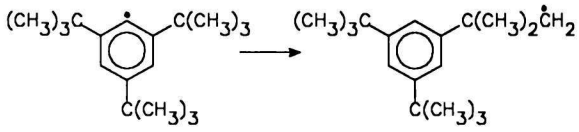
The dimensions of the barriers for the reaction H + H_2 were determined by the BEBO (bond energy—bond order) method [8, 9] using the classical and vibrational-adiabatic approximations [10]. Further, T_c and $\Gamma(T)$ calculations were carried out for Shavitt's classical barrier [11] and for the classical and vibrational-adiabatic barriers obtained by *Truhlar* and *Kuppermann* [10] from SSMK surface [12]. The corresponding values of V_0 are listed in Table 1. For the reaction paths [10, 11], the half-width of the barrier ℓ is calculated from the relationship for curvature $F = 2V_0/\ell^2$ [7].

Table 1. Characteristic Temperatures T_c for the Reaction H + H_2

Potential barrier	V_0 / kJ mol^{-1}	T_c/K eqn (*1*)	eqn (*2*)	eqn (*3*)
BEBO	50.02	255.0	510.0	462.5
VA-BEBO[a]	43.15	242.5	485.5	439.9
SB[b]	40.91	207.0	414.0	375.4
TK barrier[c]	40.91	207.0	414.0	375.4
VA-TK[d]	26.75	167.4	334.7	303.6

a) Vibrational-adiabatic BEBO method; *b*) Shavitt's barrier; *c*) Truhlar—Kuppermann's barrier; *d*) vibrational-adiabatic treatment of the Truhlar—Kuppermann's barrier.

The isomerization of 2,4,6-tri-*tert*-butylphenyl radical occurs *via* the intramolecular 1,4 H transfer



The rate constants have been measured in the range of 113—247 K and strong isotopic effects have been observed [13]. The Arrhenius plot is curved and below 170 K the rate constant varies only slightly with temperature. Fitting the equation for the rate constant calculation to the experimental data, for the height and half-width of the barrier the following values have been obtained [13]: V_0 = 60.7 kJ mol^{-1} and ℓ = 0.033 nm for Eckart's barrier, and V_0 = 58.6 kJ mol^{-1} and ℓ = 0.0395 nm for Gauss' barrier. For the reaction

Table 2. Input Parameters for the BEBO Method

Parameter	i[a] 1	2	3
D_i/(kJ mol^{-1})	426.8	443.5	353.5
r_i 10^{10}/m	1.092	1.086	1.507

a) Indices i = 1, 2, 3 correspond to the bond being broken, being formed and the bond between the atoms where the transfer reaction occurs. D_i and r_i are the dissociation energy and the equilibrium distance of the i-th bond. The values of parameters p, q, and β are: p = 1.08210, q = 1.08410, β = 1.94 x 10^{10} m^{-1}.

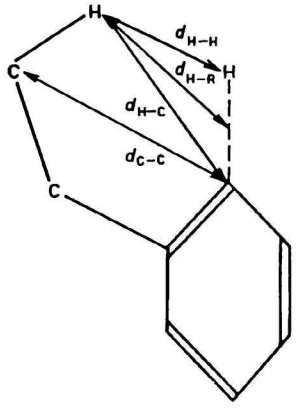


Fig. 1. A part of the molecule of 2,4,6-tri-*tert*-butylphenyl radical with the hydrogen transfer path considered.

system under investigation having a relatively great number of atoms we calculated the potential barrier dimensions (V_0, ℓ) by the modified BEBO method [14]. The input parameters for the method are listed in Table 2. In this way, the value V_0 = 61.84 kJ mol^{-1} has been obtained. For the BEBO method, it is a pretty complex task to perform the transformation from the bond orders to the distance coordinate. For this reason, we made a trial to estimate d as the distance which H atom has to pass from the equilibrium configuration of reactant to that of the product. Under the assumption that the best configuration for H atom transfer in 2,4,6-tri-*tert*-butylphenyl radical occurs in the moment of the formation of the five-membered planar activation complex, d was estimated from the interatomic distances in the radical. We took into account four distances (Fig. 1), the values of d are listed in Table 3. For the TFP model, the half-width of the potential barrier was taken as $\ell = d/2$ and ω was the frequency of oscillation of the particle of mass μ in the potential well having the curvature F

$$\omega = 2\pi\nu = (F/\mu)^{1/2} = (2V_0/\ell^2\mu)^{1/2} \qquad (6)$$

As the reaction is not athermic, the asymmetry of the potential barrier was calculated as $\Delta V = D_1 - D_2 = -16.66$ kJ mol^{-1}, where D_1 and D_2 are dissociation energies of the bond being broken and formed, respectively, calculated by Benson's method of group additivity [15].

For model reaction sets, the values of V_0, ΔV, ω, and ℓ were varied within the range of their usual magnitudes in H atom transfer reactions. Set I (TFP model) involves three intermolecular transfer reactions with constant value ℓ = 0.05 nm and V_0 = 41.86 kJ mol^{-1} The calculations of $\Gamma(T)$ and T_c were carried out for three values of the potential barrier asymmetry (Table 4). The calculation of T_c according to eqn (4) was performed for the reactions of set II (Fig. 2) with the aim of demonstrating the dependence of T_c on ΔV, ω, and d (model TBP).

Table 3. Characteristic Temperatures Calculated by Eqns (*1*–*4*) for the Isomerization of 2,4,6-Tri-*tert*-butylphenyl Radical (V_0 = 61.84 kJ mol^{-1}, μ = 1 m_u, ΔV = – 16.66 kJ mol^{-1}, $\ell = d/2$)

Distance	$d \cdot 10^{10}$	$\omega \cdot 10^{-13}/2\pi$	T_c/K			
	m	s^{-1}	eqn (*1*)	eqn (*2*)	eqn (*3*)	eqn (*4*)
d_{H-H}	1.44	2.46	187.5	374.5	340.3	361.9
d_{H-R}[a]	1.76	2.01	153.4	306.7	278.4	292.9
d_{H-C}	2.25	1.57	119.9	239.9	217.8	226.7
d_{C-C}	2.78	1.27	97.1	194.2	176.3	182.2

a) R is the centre of the C—H bond (Fig. 1).

Table 4. Tunneling Factors $\Gamma(T)$ and Characteristic Temperatures for the Model Reactions Set I (V_0 = 41.86 kJ mol^{-1}, ℓ = 0.05 nm, μ = 1 m_u); T_c(eqn (*1*)) = 221.6 K, T_c(eqn (*2*)) = 443.2 K, T_c(eqn (*3*)) = 401.9 K

ΔV	$\omega \cdot 10^{-13}$	Calculations	T/K						
kJ mol^{-1}	s^{-1}		220	280	400	520	640	880	1000
–12.56	3.10	*a*	19.7	12.5	6.7	4.3	3.2	2.2	1.9
	3.10	*b*	55.9	5.4	1.9	1.4	1.3	1.1	1.1
	9.71	*c*	13.9 x 10^6	11.6 x 10^4	707.0	55.9	13.8	3.7	2.7
	9.71	*d*	1.0 x 10^6	1.2 x 10^4	164.0	23.0	8.3	3.2	2.5
0	2.90	*a*	17.5	11.2	5.9	3.9	2.9	2.0	1.8
	2.90	*b*	24.2	4.0	1.8	1.4	1.2	1.1	1.1
	9.11	*c*	91.5 x 10^5	77.6 x 10^3	491.0	41.0	10.8	3.2	2.4
	9.11	*d*	3.2 x 10^5	5.1 x 10^3	91.6	15.9	6.5	2.9	2.3
12.56	2.66	*a*	14.7	9.4	5.1	3.4	2.6	1.9	1.7
	2.66	*b*	8.9	3.0	1.6	1.3	1.2	1.1	1.1
	8.30	*c*	47.3 x 10^5	41.1 x 10^3	278.0	25.7	7.6	2.7	2.1
	8.30	*d*	1.0 x 10^4	5.0 x 10^2	31.4	8.8	4.5	2.3	2.0

a – Wigner's corrections (eqn (*7*)), *b* – calculation according to eqn (*8*) with F taken from eqn (*9*), *c* – calculation according to eqn (*8*) with F taken from eqn (*10*), *d* – calculation for Eckart function.

Transmission Probabilities and Tunneling Factors

Since the tunneling factors are originally defined for the TFP model, we calculated them and also the transmission probabilities only for $H + H_2$ reaction and for the model reactions set I.

The calculation of transmission probabilities $P(E)$ can be carried out in two ways, *i.e.* using the closed forms for $P(E)$, or using the procedure for numerical integration of Schrödinger's equation. We have used the program by *Le Roy et al.* [16, 17] based on the latter approach. Since the original program had implanted Gauss' barrier only, we have extended it for other types of barriers and, the part of program dealing with the asymmetric barriers has been treated more exactly [18].

The transmission probabilities were calculated for Eckart's barriers [19] and the tunneling factors were obtained by the numerical integration of eqn (5). Besides these exact numerical values of $\Gamma(T)$ for Eckart's barrier, the calculations of Wigner's tunneling corrections [7] $\Gamma_w(T)$ were carried out

$$\Gamma_w(T) = 1 + [(h\nu/k_BT)^2/24] \qquad (7)$$

where ν is defined by eqn (6). The calculation of tunneling factors according to Bell's formula [7] was made as well

$$\Gamma(T) = \pi\alpha/(\beta \sin(\pi\alpha/\beta)) - \alpha\, e^{\alpha} Y \qquad (8)$$

where $Y = e^{-\beta}/(\beta - \alpha) - e^{-2\beta}/(2\beta - \alpha) +$ and dimensionless parameters $\alpha = V_0/k_BT$, $\beta = 2\pi^2\ell(2\mu V_0)^{1/2}/h$ characterize the given barrier. Using eqn (6) in the definition of parameter β, the asymmetry and also the shape of the potential barrier can be taken into account as the calculation of ν is effected through the curvature F. Thus, we can get different results for the same barrier dependent on the F calculation. For illustration, for the same values of V_0, ℓ, and ΔV we used the expression of F for the asymmetric parabola [7]

$$F = B/(2\ell^2) \qquad (9)$$

and for Eckart's barrier [20]

$$F = \pi^2(\Delta V^2 - B^2)^2/(2B^3\ell^2) \qquad (10)$$

where $B = (V_0^{1/2} + (V_0 - \Delta V)^{1/2})^2$ and the values of ν and $\Gamma(T)$ calculations according to eqn (8) are listed in Table 4. Use of solely the first term of eqn (8) is admissible only for $\alpha/\beta \ll 1$. This condition is not always satisfied, therefore the $\Gamma(T)$ calculation was repeated till the difference between two steps was less than 0.01 %. This procedure has been also inserted into the original Le Roy's program [16, 17].

For $H + H_2$ reaction, our aim has been to compare the T_c and $\Gamma(T)$ criteria. Therefore, the calculations of $P(E)$ and $\Gamma(T)$ were carried out for all the five reaction paths (Table 5).

Reduced Mass of Tunneling Particle

It is generally known [7] that the reduced mass of the tunneling particle μ strongly affects both T_c and $\Gamma(T)$. For the sake of simplicity, in our calculations μ is considered to be constant for all the reaction coordinates. For the reaction $H + H_2$ it was taken $\mu = m_H/3$, where m_H stands for the mass of H atom [7]. In the other cases we supposed that H atom transfer occurs between much heavier atoms (C or O) and, consequently, $\mu = m_H$.

DISCUSSION

Reaction H + H_2

This reaction has been studied experimentally several times (see Refs. [21, 22] and references quoted therein). The Arrhenius activation energy has been estimated as $E_A = 34.1$ kJ mol^{-1} and a slightly curved Arrhenius plot has been observed [21] for temperatures $T < 340$ K, which corresponds rather to small tunneling contributions than to moderate or large ones. In this case, it would have to be $\Gamma(T) \ll 4$ for temperatures $T > 340$ K and $T = 340$ K would have to fall to the interval $(T_c, 2T_c)$. As can be seen from Tables 1

Table 5. Tunneling Factors $\Gamma(T)$ for the Reaction $H + H_2$

T/K	BEBO	VA-BEBO	SB	TK	VA-TK
160	0.537×10^6	0.388×10^5	0.112×10^3	0.179×10^3	1.788
220	0.555×10^3	0.118×10^3	8.634	0.114×10^2	1.241
280	0.290×10^2	0.135×10^2	3.524	4.198	1.107
340	7.336	4.018	2.318	2.616	1.052
400	3.608	2.375	1.835	2.008	1.025
460	2.404	1.763	1.588	1.703	1.010
640	1.408	1.196	1.281	1.333	0.993
820	1.163	1.046	1.171	1.202	0.987
1000	1.066	0.988	1.117	1.138	0.986

and 5, both criteria overestimate the role of tunneling and a better agreement with experimental data is reached for the vibrational-adiabatic versions of barriers [10, 11] in comparison with their classical analogues. However, both T_c and $\Gamma(T)$ strongly depend on the accuracy of the estimation of potential barrier dimensions. There also exist serious differences between the values of T_c calculated according to eqns (*1*—*3*), where the first equation gives more acceptable T_c values.

Model Reaction Set I

As it follows from eqns (*1*—*3*), the critical temperature for the TFP model is independent of the potential barrier asymmetry. For V_0 = 41.86 kJ mol^{-1} and ℓ = 0.05 nm, the values T_c = 221.6 K, 443.2 K, and 401.9 K were obtained from eqns (*1*—*3*), respectively. The $\Gamma(T)$ values shown in Table 4 reveal that, for the asymmetric barriers, the tunneling contributions decrease for the endothermic reactions and increase for the exothermic ones. This result is in agreement with *Harmony*'s assumption [23] and, of course, it is in contradiction with *Bell* [7] who assumed that the maximum $\Gamma(T)$ values are reached for ΔV = 0. We are of the opinion that, for drawing conclusions based on the region available for tunneling in reactions as it has been done in Ref. [7], the barriers of the same values V_0 and ℓ (and different ΔV) should be subjected to the investigation.

Considering the tunneling corrections, eqn (*7*) has been derived [7] under the condition that $h\nu/k_BT \leq 2$. The temperature, at which this condition is satisfied, depends on the way of F and v expression. For the calculation of F and v by eqn (*9*) or eqn (*10*) this situation takes place at $T \geq 700$ K or at $T > 1400$ K. Since V_0, ℓ, and ΔV have been chosen from the interval of their usual values in H atom transfer reactions, we have come to the conclusion that Wigner's corrections are not defined for the temperatures where the contributions of tunneling are expected to be great and, consequently, they are unapplicable as tunneling criteria. $\Gamma(T)$ calculated according to various approaches (Table 4) give often the values differing by orders and this strong dependence of the results on the method lowers the reliability of the predictions drawn from $\Gamma(T)$ calculations.

Comparison of T_c and $\Gamma(T)$ (Table 4) shows that the predictions do not coincide. In the case of T_c, great tunneling contributions should occur (T_c = 401.9 K) for $T \leq 201$ K. In contrast with that, the $\Gamma(T)$ values predict the interval 300—800 K in the dependence on the way of calculation. Thus, it is necessary to keep in mind the mentioned features of T_c and $\Gamma(T)$ when using these criteria for the predictions of the tunneling contribution in chemical reactions.

Model Reactions Set II

The results of calculations are shown in Fig. 2. Comparing the results with those listed in Tables 1 and 4, the difference between the TFP and TBP models is distinct. For example, the dependence of T_c on d for the TBP model is not linear (curve *1*) and the dependence of T_c on ΔV (curve *2*) can be depicted by the two symmetrical parabolas having the axis of reflection collinear with the axis of temperature and passing through the point of singularity with ΔV = 0 (for eqn (*4*)). This behaviour is obviously a consequence of the solution of the transcendental equation (*5*) in Ref. [6]. The dependence of T_c on ω (curve *3*) exhibits a singular point (but no symmetry).

Besides the mentioned limitation of eqn (*4*), our calculations point out that reasonable results are reached only for $q \geq 2p$ and $q < p$. Generally, the T_c calculation for the TBP model is highly sensitive to the choice of all three input parameters and the calculations often skip over the region of validity of eqn (*4*), mainly for $d < 0.05$ nm and $\omega < 10^{12}$ s^{-1}. Also, a certain disadvantage is that eqn (*4*) cannot be used for ΔV = 0 and that the q and p values have to be continuously tested.

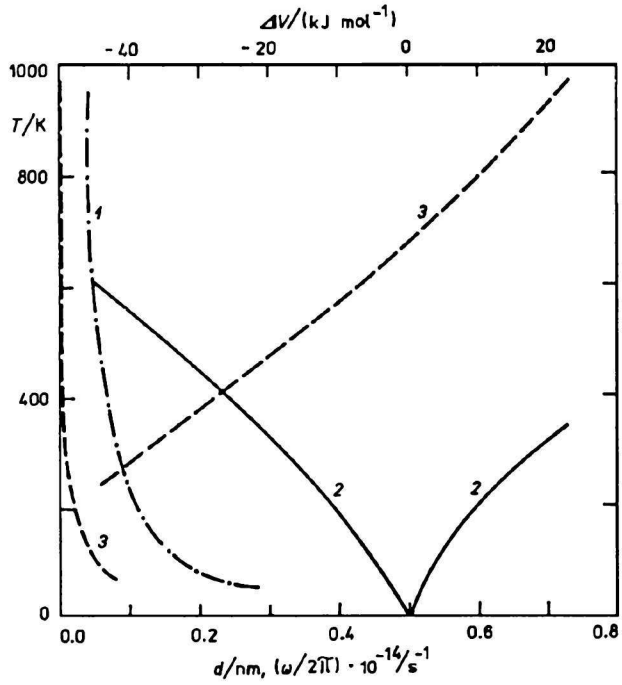


Fig. 2. Dependence of the characteristic temperature on various parameters for the model of the tunneling bonding particle. *1*. T_c = f(d); *2*. T_c = f(ΔV); *3*. T_c = f(ω).

Isomerization of 2,4,6-Tri-*tert*-butylphenyl Radical

Table 3 shows an excellent agreement between the height of the potential barrier that we obtained by the BEBO method and the height obtained by *Brunton et al.* [13] by fitting the rate constant equation to the experimental data. As for T_c, in this case different approaches give qualitatively the same results. Thus the application of the TFP model for similar systems will probably lead to acceptable results.

It is obvious that T_c calculated according to eqn (*2*) is twice higher than that obtained from eqn (*1*), whereas eqn (*3*) gives the values only slightly lower than eqn (*2*). Thus, the confrontation of calculated T_c values with the experimental data is needed. The Arrhenius plot can be approximated by two straight lines (see Fig. 7 in Ref. [13]). The first one corresponds to the activated high-temperature H atom transfer and the other one to the nonactivated low-temperature tunneling mechanism. The straight lines intersect at the temperature of about 170 K which represents the T_c value determined "experimentally" Below this temperature the tunneling mechanism should play an important role. The best agreement between the experimental and calculated T_c values is reached for d = 0.278 nm in the case of eqns (*2—4*) and for d = 0.144 nm for eqn (*1*), which represent the C—C and H—H distances, respectively (see Fig. 1 and Table 3). Although it is not possible to draw a far-reaching general conclusion from this sole example, it seems that for reactions studied in the framework of the TBP model the best T_c values will be obtained taking d as the distance between the equilibrium configurations of the atoms where the transfer reaction occurs.

CONCLUSION

As it follows from the results, the values of characteristic temperatures and tunneling factors strongly depend on the dimensions of potential barriers. Quality of the estimation of the barrier dimensions is often questionable since the present-time methods of potential energy surface calculations are very rarely able to provide the parameters reliable enough. Thus, the mentioned dependence reduces the reliability of the results for other systems where the barrier dimensions are not known with sufficient accuracy. The results further show that the best criterion with the possibility of application for any reaction system cannot be unambiguously determined. As it can be seen the selection of the tunneling factors as a tunneling criterion is based on experience and has no theoretical background. On the other hand, the equations for characteristic temperatures were derived under certain simplifications carrying limited usability (symmetric or asymmetric barriers, type of the model, *etc.*) and errors of the results obtained (mainly in the case of eqns (*1—3*)).

For the reactions in condensed phase (TBP model), Bruhks and Jortner's criterion [6] can be recommended for the asymmetric barriers and Christov's criterion [4, 5] (eqn (*3*)) with half-width $\ell = d/2$ for the symmetric ones. The case of H + H_2 reaction indicates that for reactions occurring in gaseous phase (TFP model) Goldanskii's criterion [1] (eqn (*1*)) is the most convenient.

It can be concluded that the predictions of tunneling contributions by the criteria mentioned above can be used only for orientation in the problem and it is necessary to keep in mind that all of them tend to overestimate the role of tunneling in chemical reactions.

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