QUANTUM MECHANICAL TUNNELLING IN THE PROCESSES $D + H_2 \rightarrow DH + H$ AND $CH_4 + H \rightarrow CH_3 + H_2$. ECKART'S TUNNELLING CORRECTIONS FOR RATE CONSTANTS GIVEN BY *ab initio* CALCULATIONS

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Dedicated to Professor E. Hála on the occasion of his 60th birthday.

Results of the best reported *ab initio* calculations are used to evaluate the rate constants of the title processes by means of the transition state theory. The computed rate constants are corrected for the quantum mechanical tunnelling by the Eckart's one-dimensional approach and comparison is made with experimental rate data.

This paper aims to contribute to the assessment of utility of the theoretical approach based on the transition state theory (TST) and *ab initio* molecular orbital calculations. A critical test[1] of that approach for a series of elementary gas-phase reactions showed that the observed rate data are well reproduced if the basis set used is of the "double zeta plus polarization" quality or better and if a large portion of the correlation energy is accounted for. These two requirements are unavoidable if a meaningful energy of activation is to be obtained which is the crucial point in the whole MO approach to the TST rate constants. Nevertheless, even with so sophisticated calculations, the predicted rate constants may differ appreciably from the observed ones at lower temperatures. *Ab initio* theorists assign usually the discrepancy to the "missing" part of the correlation energy. Their estimates of the "true" energy barrier, however, are mostly rough because they disregard quantum mechanical tunnelling and sometimes they use the Arrhenius activation energy as a standard. In this paper a more rigorous treatment is presented for the processes $D + H_2 \rightarrow DH + H$ and $CH_4 + H \rightarrow CH_3 + H_2$ which should show more realistically the present state of art in the field of applications of nonempirical MO calculations to the problems of chemical reactivity.

THEORETICAL

The rate constants were evaluated by the common TST expression for a bimolecular reaction

$$k = \Gamma l \frac{kT}{h} \frac{Q^{\neq}}{Q_A Q_B} \exp\left(-\Delta H_0^{\neq}/RT\right), \qquad (1)$$

where Q_A and Q_B are partition functions of reactants, $Q^{\neq}$ is the partition function of the activated complex, $\Delta H_0^{\neq}$ is the enthalpy of activation at absolute zero, l is the statistical factor[2] and Γ is the tunnelling correction factor. Partition functions were constructed within the rigid rotor – harmonic oscillator (RRHO) approximation assuming ideal gas behaviour of both reactants and transition state species. All quantities necessary for the evaluation of the expression (*1*) originated from *ab initio* calculations (*vide infra*). The tunnelling correction factor was calculated according to the Eckart's approach[3] to the one-dimensional quantum mechanical tunnelling but with the modifications advocated by Jakubetz[4] for one-dimensional reactions. In our case this means that the height of the Eckart's barrier was set equal to $\Delta H_0^{\neq}$ and the imaginary frequency (corresponding to the vibrational mode with the negative eigenvalue and determining the width of the Eckart's barrier) was corrected as follows

$$h\nu_E = h\nu_S \sqrt{(\Delta H_0^{\neq}/E_c)}, \qquad (2)$$

where ν_S is the imaginary frequency obtained directly from the vibrational FG analysis of the transition state and E_c is the "classical" energy of activation, *i.e.*, the energy barrier given directly by *ab initio* calculations.

RESULTS

The Process $D + H_2 \rightarrow DH + H$

The TST treatment of this process based on the best *ab initio* data[5] was communicated by Koeppl[6]. In contrast to Koeppl, for the energy barrier use was made in the present paper of the value of 41·0 kJ/mol given directly by the Liu's calculations[5] instead of the estimated lower bound of 39·7 kJ/mol or the rigorous upper bound of 43·0 kJ/mol. Some ambiguity is met with the zero-point energy of H_2. One may use the energy of the vibrational ground state, or, in the spirit of the RRHO approximation, the zero-point energy may be assumed as a half of the $0 \rightarrow 1$ transition energy. We favoured the second possibility in order to be consistent with the treatment for H_3. A complete list of data necessary for the TST treatment is presented in Table I. The result is presented in Fig. 1. The dashed line represents the temperature dependence of the computed TST rate constant. It lies between the Koeppl's upper and lower bounds in the whole temperature range assumed. The TST treatment is unsatisfactory in the following points: it does not reproduce the curvature of the temperature dependence, it underestimates drastically the reaction rate at low temperatures, and even in the high temperature range the reaction rate is somewhat underestimated. In accordance with the common assumption about negligible tunnelling at high temperatures, Koeppl concluded[6] that a true classical activation energy should be close to the lower bound (39·7 kJ/mol) estimated by Liu. The full line in Fig. 1 suggests a different explanation. It is seen that upon applying the tunnelling correction, excellent agreement with experiment is obtained except for the low temperature region. A failure of the Eckart's approach at low temperatures is very common, the main reason for it being the fact that the Eckart's function is determined by the characteristics of the transition state so that it may deviate considerably from the reaction coordinate in the entrance part of the reaction valley. At low temperatures, of course, the quantum mechanical tunnelling occurs mainly just in that part of the reaction valley.

TABLE I

Data Used for the Treatment of the Process $D + H_2 \rightarrow DH + H$

Quantity	Its value	Origin
B_0 for H_2	59·334 cm^{-1}	[a]
DH and HH bond lengths in DH_2	0·9297 . 10^{-10} m	[b]
Vibrational wavenumber $\nu_0 \rightarrow 1$ for H_2	4 161·16 cm^{-1}	[a]
Force constants for DH_2: stretching	102 Nm^{-1}	[b]
stretch-stretch interaction	147 Nm^{-1}	[b]
bending	8·14 . 10^{-20} Nm/Rad^2	[c]
Vibrational modes for DH_2: imaginary	1 430·3 cm^{-1}	[d]
bending	933·9 cm^{-1}	[d]
stretching	1 762·8 cm^{-1}	[d]
Zero point energy for H_2 assumed as $\frac{1}{2}(\nu_0 \rightarrow 1)$	24·9 kJ/mol	[a]
Zero point energy for DH_2	21·7 kJ/mol	[e]
Classical barrier height, E_c	41·0 kJ/mol	[b]
Enthalpy of activation, $\Delta H_0^{\ddagger}$	37·8 kJ/mol	[f]
Imaginary wavenumber for Eckart's tunnelling	1 373·3 cm^{-1}	[g]

[a] Ref.[7]; [b] Ref.[5]; [c] Ref.[8]; [d] FG matrix analysis for the tabulated force constants; [e] From the tabulated wavenumbers; [f] From E_c and zero-point energies; [g] Eq. (2).

The Process $CH_4 + H \rightarrow CH_3 + H_2$

The best *ab initio* calculations for this process were communicated by Niblaeus and collaborators[11]. In these calculations the optimum geometry and the classical activation energy were computed for the assumed axial C_{3v} activated complex H_3CHH. From the reported energies[11] for points lying close to the anticipated reaction path at the top of the activation barrier, we obtained by a harmonic fit the force constants for the critical CH and HH bonds. From them we arrived at the "imaginary" vibrational frequency needed for the Eckart's tunnelling. The other vibrational modes of CH_5 were obtained from the harmonic force constants given by the SCF 4-31G calculations[12]. Since the wavenumbers so determined are likely to be open to some uncertainties, we selected for CH_4 the data[13] given by the same approach so that a certain cancellation of errors in the TST treatment may be expected. The complete set of quantities needed in the TST treatment is listed in Table II. The computed rate constants are presented in Fig. 2. Again, the Eckart's tunnelling correction improves the agreement with experiment. If use is made of a fit[17] to experimental data, $k = 6{\cdot}25 \,.\, 10^{13} \exp(-48\,600 \text{ J mol}^{-1}/\boldsymbol{RT})$, the TST prediction for the rate constant

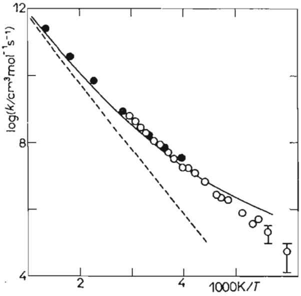

FIG. 1

Temperature Dependence of the Rate Constant for the Process $D + H_2 \rightarrow DH + H$

The dashed and full lines, respectively, represent the TST treatments without and with applying the Eckart's correction for the quantum mechanical tunnelling. Experimental data are taken from ref.[9] (●) and ref.[10] (○).

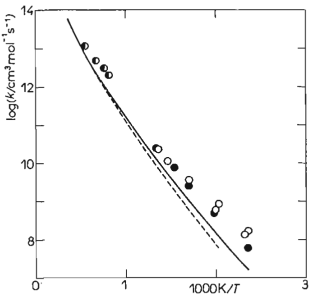

FIG. 2

Temperature Dependence of the Rate Constant for the Process $CH_4 + H \rightarrow CH_3 + H_2$

The dashed and full lines, respectively, represent the TST treatments without and with applying the Eckart's correction for the quantum mechanical tunnelling. Experimental data are taken from ref.[15] (◐), ref.[16] (●) and ref.[17] (○).

at 298 K is underestimated by a factor of about 30 whereas if the tunnelling correction is applied, the factor reduces to ~ 5. The remaining discrepancy may be assigned to the underestimated energy barrier[11], the error being $4-6$ kJ/mol.

It is fair to note on the semiempirical TST treatment by Kurylo and coworkers[17], who made use of semiempirical BEBO and LEPS surfaces and applied the Eckart's in its original form. In spite of the simple theoretical approach used, the calculated kinetic isotope effect was in reasonable agreement with experiment.

CONCLUSIONS

The justifiability if the theoretical approach used has been the subject of many critical papers. According to them TST should be regarded as a postulate rather than a well founded "absolute" theory of rate processes[18] and also for the Eckart's approximation it was advocated[19] that its use should be avoided. However, having no alternative practical tool available for treatments of real chemical reactions, examination of the application limits of the combined approach TST + Eckart's tunnelling is still worth pursuing. It is the author's opinion that in most cases this approach is

TABLE II

Data Used for the Treatment of the Process $CH_4 + H \rightarrow CH_3 + H_2$

Quantity		Its value	Origin
CH Bond length in CH_4		$1{\cdot}093 \,.\, 10^{-10}$ m	[a]
Geometry of the activated complex $H_3CH^1H^2$:	$r_{H^1H^2}$	$0{\cdot}903 \,.\, 10^{-10}$ m	[b]
	r_{CH^1}	$1{\cdot}376 \,.\, 10^{-10}$ m	[b]
	r_{CH}	$1{\cdot}095 \,.\, 10^{-10}$ m	[c]
	$\sphericalangle$ HCH	$114{\cdot}7°$	[c]
Zero point energy for CH_4		123·1 kJ/mol	[d]
Zero point energy energy for CH_5		112·4 kJ/mol	[e]
Classical barrier heigt, E_c		67·3 kJ/mol	[f]
Enthalpy of activation, $\Delta H_0^{\ddagger}$		56·7 kJ/mol	[g]
Imaginary wavenumber for CH_5		1 400 cm^{-1}	[h]
Imaginary wavenumber for Eckart's tunnelling		1 285 cm^{-1}	[i]

[a] Ref.[14]; [b] From UHF-CI *ab initio* calculations[11]; [c] Assumed[11]; [d] Wavenumbers from the FG matrix analysis; force constants from 4-31G calculations[13]; [e] Wavenumbers from the FG matrix analysis; force constants from 4-31G calculations[12]; [f] Ref.[11]; [g] From E_c and zero-point energies; [h] As in the footnote [e] but the stretching and stretch-stretch force constants obtained from a quadratic fit to energy values given by UHF-CI *ab initio* calculations[11]; [i] Eq. (*2*).

capable of giving rate constants with the accuracy comparable to that of experiment, provided that the treatment is based on data given by highly accurate *ab initio* calculations. The results attained in this paper support this opinion.

From the practical point of view the following two conclusions may be formulated: *1*) Eckart's function with the properly selected[4] barrier height and width gives reasonable tunnelling correction factors for the reactions $D + H_2 \rightarrow DH + H$ and $CH_4 + H \rightarrow CH_3 + H_2$. This suggests that the Eckart's approximation may also be applied to processes for which the assumptions inherent to the Eckart's approach, such as *e.g.* the zero reaction path curvature, are not satisfied as well as in some collinear reactions[4]. *2*) From Fig. 2 it is possible to estimate the true activation barrier for the reaction $CH_4 + H \rightarrow CH_3 + H_2$ to ~62 kJ/mol. The barrier of 67·3 kJ/mol given by *ab initio* calculations[11] appears therefore to be in much better agreement with experiment than assumed by the cited *ab initio* theorists[11]: according to their speculative estimate based on the Arrhenius energy the computed barrier was by ~20 kJ/mol too high.

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