

LS-ISM/scTST Calculations Manual

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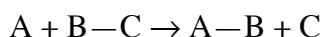
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Introduction

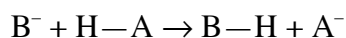
The aim of this Manual is twofold. For the expert that does not need detailed information and for the user that wishes to obtain rate estimates without spending too much time with the details, it presents an approach that should give access to rate constants of atom and proton transfers in less than 15 minutes. For the expert that wishes to know all the approximations involved in the calculations, the implementation of the algorithm and the significance of all the results, it also presents an in-depth discussion of the LS-ISM/scTST method to calculate rate constants.

14 min away from my rate constant

of an atom-transfer reaction



or a proton-transfer reaction



1) Create a data file describing your reactants and products.

The simplest way to make such a file is to download and modify one of the files provided as example. In order to download the file you want, just click on its name ([in blue](#)) and follow your browser instructions. Some browsers download the files directly to the desktop. For each example file there is a corresponding [results](#) file that you may also download the same way.

For an atom transfer use the “F+H2” file as a template.

For a proton transfer in the absence of H-bonding use the “HO-+CH2(COCH3)2” file as a template.

For a proton transfer in the presence of H-bonding use the “*ArOH+H2O” file as a template.

2) Open the downloaded file.

You can open the downloaded template using any current word processor. It is just an ASCII file.

The first line is the name of the system. You may change it to a short description of your own system.

For atom transfer follow the sequence below. For proton transfers jump to the corresponding section

Input data for atom transfers

The second line is a series of numbers:

0 0 1 1 0 1 1 1 100

The first "0" defines an atom transfer (zero charge), and all the other numbers refer to parameters that are not employed in atom-transfer calculations. They should be kept as they are.

The third line is another series of numbers:

19 1 1 104.2 4161 0.7414 136.2 3962 0.917 0 0
17.423 3.4480 13.598 0.7542 2 0 280 180

These data is appropriate for the $F + H_2 \rightarrow HF + H$ reaction. Their meaning, for an $A + B-C \rightarrow A-B + C$ reaction, is as follows

<i>Number</i>	<i>Symbol</i>	<i>Description</i>	<i>Units</i>
19	m_A	Mass of atom A	amu
1	m_B	Mass of atom B	amu
1	m_C	Mass of atom C	amu
104.2	$D_{BC,298}^0$	Bond dissociation energy of BC bond	kcal/mol
4161	$\bar{\nu}_{BC}$	Infrared stretching frequency of BC bond	cm^{-1}
0.7414	$l_{BC,eq}$	Equilibrium bond length of BC bond	Å
136.2	$D_{AB,298}^0$	Bond dissociation energy of AB bond	kcal/mol
3962	$\bar{\nu}_{AB}$	Infrared stretching frequency of AB bond	cm^{-1}
0.917	$l_{AB,eq}$	Equilibrium bond length of AB bond	Å
0	D_{0AC}	Hydrogen-bond binding energy of $A \cdots BC$	kcal/mol
0	D_{0CA}	Hydrogen-bond binding energy of $AB \cdots C$	kcal/mol
17.423	$I_p(A)$	Ionization potential of A	eV

3.4480	$E_A(A)$	Electron affinity of A	eV
13.598	$I_p(C)$	Ionization potential of C	eV
0.7542	$E_A(C)$	Electron affinity of C	eV
2	σ	Statistical factor (# equivalent B atoms)	
0	j	Scaling of the pre-exponential factor	
280	T_{av}	Average temperature to calculate activation energy	K
180	angle	A···B···C angle	degrees

Change the numbers to those corresponding to your system. A table with a large number of parameters for $D_{BC,298}^0$, \bar{v}_{BC} , $l_{BC,eq}$, $D_{AB,298}^0$, \bar{v}_{AB} , $l_{AB,eq}$, D_{0BA} , D_{0AB} , $I_p(A)$, $E_A(A)$, $I_p(C)$ and $E_A(C)$ can be downloaded from the site. The statistical factor σ is number of equivalent B atoms, which may be taken from the symmetry number of the molecule. Use $j=0$ for atom + molecule, $j=2$ for (diatomic radical) + (diatomic molecule) or (diatomic radical) + (polyatomic molecule), and $j=3$ for (polyatomic radical) + (polyatomic molecule). This scales the range of ratio of partition functions in the pre-exponential factor of TST. When $D_{0BA}>0$, you must be set $\sigma=1$ and $j=0$ because the system is calculated as an intramolecular reaction. T_{av} is the mid-range temperature of your systems and is *only* involved in the estimate of the activation energy; it is not involved in the calculation of the rate constants. Use an angle of 180 degrees as default; a smaller value will decrease the zero-point energy of the transition state, and is only recommended for intramolecular reactions.

Input data for proton transfers

The second line is a series of numbers. For the template “*ArOH+H2O->*ArO-+H3O+”, it reads:

1 2.71 1 1 -1.74 1 1 1 100

The first “1” defines an proton transfer (+1 charge), and the meaning of all the numbers, for a $B^- + H-A \rightarrow B-H + A^-$ proton transfer is as follows

<i>Number</i>	<i>Symbol</i>	<i>Description</i>	<i>Units</i>
1		Defines the system as a proton transfer reaction	
2.71	$pK_a(AH)$	Acidity constant of acid HA	
1	p_A	Number of equivalent protons in acid HA	
1	q_A	Number of equivalent basic sites in base A^-	
-1.74	$pK_a(BH)$	Acidity constant of acid HB	
1	p_B	Number of equivalent protons in acid HB	
1	q_B	Number of equivalent basic sites in base B^-	

1	K_{compl}	Equilibrium constant of precursor complex	M^{-1}
100	ΔG^0	Reaction free-energy	kcal/mol

When $pK_a(AH)$ or $pK_a(BH)$ are not known, or when you wish to calculate the rate for a specific reaction free energy, set ΔG^0 equal to the desired free-energy and the calculation will not employ the pK_a values. If you set $\Delta G^0=100$, as in the system above, the reaction free-energy is calculated from the pK_a difference of HB and AH, corrected for the statistical factors p_A , q_A , p_B and q_B . Set $K_{compl}=1$ in the absence of hydrogen bonds because the pre-exponential factor is calculated as in the case of polyatomic reactants, detailed further below. For proton transfers to/from water in aqueous solution, you must also set $K_{compl}=1$ because these are treated as first-order reactions, with the results in units of s^{-1} . You must divide the results by the concentration of water ($[H_2O]\approx 55$ M in pure water) to obtain the second order rate constant, in units of $M^{-1} s^{-1}$. Proton transfers to hydrogen-bonded bases in water when the base is not H_2O or OH^- , usually have $K_{compl} < 1 M^{-1}$. The actual value depends on the competition between H-bonding to the base and to the solvent.

The third line is another series of numbers:

16 1 16 86.5 3650 0.956 119.0 3657 0.9575 2 4
 13.017 1.8277 4.733 2.253 1 0 298 180

These data is appropriate for the $*ArOH + H_2O \rightarrow *ArO^- + H_3O^+$ reaction. Their meaning, for a $B^- + H-A \rightarrow B-H + A^-$ proton transfer is as follows

Number	Symbol	Description	Units
16	m_B	Mass of atom B	amu
1	m_H	Mass of atom H (or deuterium)	amu
16	m_A	Mass of atom A	amu
86.5	$D_{HA,298}^0$	Bond dissociation energy of HA bond	kcal/mol
3650	$\bar{\nu}_{HA}$	Infrared stretching frequency of HA bond	cm^{-1}
0.956	$l_{AH,eq}$	Equilibrium bond length of HA bond	Å
119.0	$D_{HB,298}^0$	Bond dissociation energy of HB bond	kcal/mol
3657	$\bar{\nu}_{HB}$	Infrared stretching frequency of HB bond	cm^{-1}
0.9575	$l_{HB,eq}$	Equilibrium bond length of HB bond	Å
2	D_{0BA}	Hydrogen-bond binding energy of $B \cdots HA$	kcal/mol
4	D_{0AB}	Hydrogen-bond binding energy of $BH \cdots A$	kcal/mol
13.017	$I_p(B)$	Ionization potential of B	eV

1.8277	$E_A(B)$	Electron affinity of B	eV
4.733	$I_p(A)$	Ionization potential of A	eV
2.253	$E_A(A)$	Electron affinity of A	eV
1	σ	Statistical factor (# equivalent protons)	
0	j	Scaling of the pre-exponential factor	
280	T_{av}	Average temperature to calculate activation energy	K
180	angle	A...H...B angle	degrees

Change the numbers to those corresponding to your system. A table with a large number of parameters for $D_{HA,298}^0$, $\bar{\nu}_{HA}$, $l_{AH,eq}$, $D_{HB,298}^0$, $\bar{\nu}_{HB}$, $l_{BH,eq}$, D_{0BA} , D_{0AB} , $I_p(B)$, $E_A(B)$, $I_p(A)$ and $E_A(A)$ can be downloaded from the site. The number of equivalent B atoms is also the symmetry number of the molecule. Use $j=0$ for atom + molecule, $j=2$ for (diatomic radical) + (diatomic molecule) or (diatomic radical) + (polyatomic molecule), and $j=3$ for (polyatomic radical) + (polyatomic molecule). This scales the range of ratio of partition functions in the pre-exponential factor of TST. Use also $j=0$ for a H-bonded system, because in this case the pre-exponential factor is the frequency of the H-bond vibration. T_{av} is the mid-range temperature of your systems and is *only* involved in the estimate of the activation energy; it is not involved in the calculation of the rate constants. Use an angle of 180 degrees as default; a smaller value will decrease the zero-point energy of the transition state, and is only recommended for intramolecular reactions.

For both atom and proton transfers the following formats have the same meaning

The fourth line is a label. Any small string can be used and does not affect the calculations

The fifth line is the temperature and the experimental rate. The temperature is expressed in Kelvin. Any value different from zero can be written in the place of the experimental rate because this parameter is not involved in the calculations.

The subsequent lines repeat the meaning of the two lines above. The time required for the calculation increases by less than a second for each temperature.

3) Save the your file

Your file must be saved an ASCII file. The most common word processors call such formats “text only” or “simple text”, and a file extension “.txt” is often used. You may save it in any folder or in the desktop.

4) Choose file

Upload your file following your browser instructions.

5) Run the calculations

Press the “Calculate” button and follow the browser instructions. Some browsers will immediately download the results file to you desktop and identified it with the date and time of the calculation. Other browsers will prompt you for a file name and a folder to save it.

5) Read the results file

If you used one of the example files, the file you obtained must be identical to the corresponding [result](#) file that you can download. The most common word processors can be used to open your results file.

Your results file consist of 5 blocks of information

The first block has only one line and is your “label”.

The second block contains many details of the calculations, described below. If you are not interested in details, just make sure that the answer to the question “did all the roots converge?” is “Y”, and then jump to the third block. If the answer is “N” verify you data file for unphysical parameters.

The details of the second block are:

The first line informs on the success in finding all the solutions for the equations, the “discontinuity” reports on the smoothness of the adiabatic reaction path at the transition state, and the “localization of $s=0$ ” tells where the transition state was located /the default is at the maximum of the classical reaction paths, but for numerical reasons it may be located at maximum of the vibrationally-adiabatic path).

The second line informs on the location of the several maxima, in terms of bond orders.

The third line informs on the location of the several minima, in terms of bond orders.

The fourth line gives the calculated electrophilicity index (m), the sum of bond extensions from reactants and products to the transition state (d), the angle employed in the calculations, and the calculated activation energy (E_{calc}) without tunneling corrections.

The fifth line gives the spectroscopic Morse constants and electronic dissociation energies.

The sixth line gives the bond order of precursor and successor H-bonded complexes.

The seventh line gives the H-bond stretching frequencies (“freq_{AC}“ and “freq_{CC}“), electronic dissociation energies and equilibrium bond lengths.

The eighth line gives the symmetric stretching frequency, and the curvatures of the classical reaction path and of the vibrationally-adiabatic reaction path at the classical transition state.

The ninth line gives the energy of the several maxima relative to the classical energy of the reactants.

The tenth line gives the energy of the several minima relative to the classical energy of the reactants.

The eleventh line gives the adiabatic reaction energy and the zero-point energies of reactants and products.

Twelfth line gives the vibrationally-adiabatic and classical barriers.

The third block is a table with labels and numbers. Their meaning is as follows:

<i>Label</i>	<i>Meaning</i>	<i>Units</i>
T	Temperatures selected for the calculation	K
ATST	Pre-exponential factors of TST	dm ³ / (mol s)
k thermal	Classical rate constants, including zero-point energy effects	dm ³ / (mol s)
tunnel corr.	Tunneling corrections, using the semiclassical approximation	
k semicl	Semiclassical rate constants, with tunneling correction	dm ³ / (mol s)

In intramolecular proton transfers or transfers to water as a solvent, the rate constants are expressed in s⁻¹.

The fourth block is 1000/T, and is provided for plotting the results

The fourth block is log(k semicl), and is provided for plotting the results

The last 3 (very long) blocks give the LS-ISM reaction coordinate, and are provided for plotting.

The first block is the reaction coordinate *s* expressed in Å, the second block is the classical reaction path expressed in kJ/mol, and the last block is the vibrationally-adiabatic reaction path expressed in kJ/mol. Please note that in the results file the units of the reaction paths are in kJ/mol, but all the other energy units are in kcal/mol.

You have your rate constants

Thank you for using ISM. The following section gives detailed information on the method and its implementation

Algorithm for LS-ISM/scTST calculations

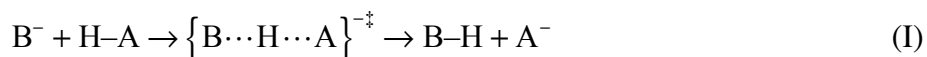
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1) Semiclassical Transition State Theory treatment of bimolecular rate constants

According to the transition-state theory (TST), the reaction rate constant of the prototypical proton transfer reaction



has the semiclassical expression

$$k_{scTST} = \kappa(T) \sigma \frac{k_B T}{h} \frac{Q^\ddagger}{Q_B Q_{HA}} e^{-\Delta V_{ad}^\ddagger / RT} \quad (1)$$

where $\kappa(T)$ is the tunneling correction, σ is the statistical factor that accounts for the degeneracy of the reaction path, Q^\ddagger , Q_A and Q_{BC} are the partition functions of the transition state and reactants, respectively, and ΔV_{ad}^\ddagger is the vibrationally-adiabatic barrier.

The first approximation is the reduction of dimensionality from polyatomic to linear triatomic systems. The partition functions of a linear triatomic system are

$$\frac{Q^\ddagger}{Q_A Q_{HB}} = \frac{q_t^\ddagger q_r^\ddagger q_{v,sym}^\ddagger (q_{v,bend}^\ddagger)^2}{q_t^A q_t^{HB} q_r^{HB} q_v^{HB}} \quad (2)$$

where q_t , q_r and q_v are the translational, rotational and vibrational partition functions, respectively. The latter explicitly acknowledge the symmetric stretching and the two degenerate bendings at the transition state. The antisymmetric stretching is the reaction coordinate. The electronic partition-functions are equal to the degeneracy of the ground state and are not included in this ratio. The partition-function ratio when a diatomic species (eg. OH⁻) attacks a polyatomic one (eg. H₂O) is the product of eq (2) by $(q_v/q_r)^2$, and when a polyatomic species (eg. H₃O⁺) attacks another polyatomic species it is the product of eq (2) by $(q_v/q_r)^3$. Hence, for the general polyatomic reaction eq (1) can be written¹

$$k_{scTST} = \kappa(T) \frac{k_B T}{h} \frac{Q^\ddagger}{Q_A Q_{BC}} \frac{\sigma}{\theta^j} e^{-\Delta V_{ad}^\ddagger / RT} \quad (3)$$

where $\theta=(q_r/q_v)$ and $j=0, 2$ or 3 for the attack of monoatomic, diatomic or polyatomic species. In this work, we assume that, for spectator modes, the value of the rotational partition function is 3 times larger

than that of the vibrational one, and treat all the systems as polyatomic, thus $\theta^j=27$.

Insertion of the partition functions of a linear triatomic system in eq (3) and making appropriate cancellations give

$$k_{sc} = A \exp\left(-\frac{\Delta V_{ad}^\ddagger}{RT}\right)$$

$$A = \kappa(T) \frac{6.82 \times 10^{10}}{\sqrt{T}} \left(\frac{m_B + m_H + m_A}{m_B(m_H + m_A)}\right)^{3/2} \frac{I_{BHA}}{I_{HA}} \frac{1 - \exp\left(\frac{\bar{\nu}_{HA} hc}{k_B T}\right)}{\left[1 - \exp\left(\frac{\bar{\nu}_{sym} hc}{k_B T}\right)\right] \left[1 - \exp\left(\frac{\bar{\nu}_{bend} hc}{k_B T}\right)\right]^2} \frac{\sigma}{27} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

(4)

where I_{BHA} and I_{HA} are the moments of inertia of the transition state and of the reactants, respectively,

$$I_{BHA} = m_B \left(l_{HB}^\ddagger\right)^2 + m_A \left(l_{HA}^\ddagger\right)^2 - \frac{\left(m_B l_{HB}^\ddagger - m_A l_{HA}^\ddagger\right)^2}{m_B + m_H + m_A}$$

$$I_{HA} = \frac{m_H m_A}{m_H + m_A} \left(l_{HA,eq}\right)^2$$

(5)

The expression for I_{HA} yields a pre-exponential factor for D^+ transfer that is half of that for H^+ transfer. This is an artifact of the simplifications introduced and is corrected in the calculations. The pre-exponential factor of deuteron transfer is assumed to be identical to that of proton transfer.²

This Manual presents the background for the calculation of l_{HB}^\ddagger , l_{HA}^\ddagger , $\bar{\nu}_{sym}$, $\bar{\nu}_{bend}$, ΔV_{ad}^\ddagger and $\kappa(T)$ using the reaction path of the Intersecting/Interacting State Model (ISM).

2) Modified Morse curves

The classical reaction path of the prototypical proton transfer is written in terms of the product bond order $n=n_{HB}$, and assumes the conservation of the total bond order, $n_{HA}+n_{HB}=1$. According to the Intersecting/Interacting State Model (ISM), the energy changes along this reaction coordinate are given by

$$V_{cl}(n) = (1-n)V_{HA}(1-n) + nV_{HB}(n) + n\Delta V^0$$

(6)

where V_{HA} and V_{HB} are the modified Morse curves of reactants and product bonds, respectively, and ΔV^0 is the reaction energy. The classical reaction energy of an atom transfer in the gas phase is $\Delta V^0 = D_{e,HA} - D_{e,HB}$, where $D_{e,HA}$ and $D_{e,HB}$ are the electronic dissociation energies of the HA and HB bonds, respectively. For a proton transfer in solution, the actual reaction (free-)energy is directly given by the pK_a difference of the

AH and BH acids. However, this requires the correction for the zero-point energy changes along the reaction coordinate, discussed further below.

The potential-energy functions employed in the ISM reaction path are Morse curves. Using the electrophilicity index of Parr³

$$m = \frac{I_p + E_A}{I_p - E_A} \quad (7)$$

where I_p and E_A are ionization potentials and electron affinities, respectively, the modified Morse curves have the form

$$\begin{aligned} V_{HA} &= D_{e,HA} \left\{ 1 - \exp \left[\beta_{HA} (l_{HA} - l_{HA,eq}) / m \right] \right\}^2 \\ V_{HB} &= D_{e,HB} \left\{ 1 - \exp \left[\beta_{HB} (l_{HB} - l_{HB,eq}) / m \right] \right\}^2 \end{aligned} \quad (8)$$

where the bond extensions are related to the bond orders using a generalization of Pauling's equation

$$\begin{aligned} l_{HA} - l_{HA,eq} &= a'_{sc} (l_{HA,eq} + l_{HB,eq}) \ln(1-n) \\ l_{HB} - l_{HB,eq} &= a'_{sc} (l_{HA,eq} + l_{HB,eq}) \ln(n) \end{aligned} \quad (9)$$

and $a'_{sc}=0.182$ is a "universal" scaling constant.¹ The equilibrium bond length, the bond dissociation energy and the vibration frequency of a given bond define its Morse curve. The depth of the potential minimum (D_e) employed in the Morse curve is calculated from the bond dissociation energy tabulated at 298 K (D^0_{298}), using the correction for the bond strength at the temperature of absolute zero and the correction for the zero-point energy,^{4,5}

$$D_e = D^0_{298} - 1.5RT + 0.5hc\omega_e = D^0_{298} - 1.5RT + 0.00143\omega_e \quad (10)$$

where the energies are expressed in kcal mol⁻¹ when the equilibrium stretching frequency (ω_e) is in cm⁻¹, and $T=298$ K to be consistent with D^0_{298} . This frequency is related to the observed infrared stretching frequency

$$\omega_e = \bar{\nu} + 0.5hc \frac{(\bar{\nu})^2}{D^0_{298} - 1.5RT} = \bar{\nu} + 0.00143 \frac{(\bar{\nu})^2}{D^0_{298} - 1.5RT} \quad (11)$$

Finally, the spectroscopic constant of the Morse curve

$$\beta = \omega_e \sqrt{\frac{2\pi^2 c \mu}{hD_e}} = 0.00651 \omega_e \sqrt{\frac{\mu}{D_e}} \quad (12)$$

is expressed in Å⁻¹ when ω_e is in cm⁻¹, D_e is in kcal mol⁻¹ and μ is the reduced mass of the directly bonded atoms, expressed in amu.

3) Classical reaction path

In terms of the modified Morse curves, the classical reaction path is

$$V_{cl}(n) = (1-n)D_{e,HA} \left\{ 1 - \exp\left[\alpha_{AH} \ln(1-n)\right] \right\}^2 + nD_{e,HB} \left\{ 1 - \exp\left[\alpha_{HB} \ln(n)\right] \right\}^2 + n\Delta V^0$$

$$\alpha_{HA} = \frac{a'_{sc} (l_{HA,eq} + l_{HB,eq}) \beta_{HA}}{m}$$

$$\alpha_{HB} = \frac{a'_{sc} (l_{HA,eq} + l_{HB,eq}) \beta_{HB}}{m}$$
(13)

and its first derivative

$$\frac{\partial V_{cl}(n)}{\partial n} = D_{e,AH} \left[1 - (1-n^\ddagger)^{\alpha_{AH}} \right] \left[(2\alpha_{HA} + 1)(1-n^\ddagger)^{\alpha_{HA}} - 1 \right] + D_{e,HB} \left[1 - (n^\ddagger)^{\alpha_{HB}} \right] \left[1 - (1 + 2\alpha_{HB})(n^\ddagger)^{\alpha_{HB}} \right] + \Delta V_{cl}^0 = 0$$
(14)

locates its transition state. The classical transition state bond order (n^\ddagger) together with eq (9) gives the geometry of the transition state, l_{HA}^\ddagger and l_{HB}^\ddagger , necessary to calculate its moment of inertia.

4) Vibrationally-adiabatic path

The classical reaction path of an atom transfer reaction, eq (6), is augmented by zero-point energy corrections along the reaction coordinate n , $Z(n)$, to yield the vibrationally-adiabatic path

$$V_{ad}(n) = V_{cl}(n) + Z(n)$$
(15)

As mentioned before, in the course of this transformation the classical reaction energy ΔV_{cl}^0 is expressed in terms of the experimental reaction free-energy corrected for zero-point energy changes between products and reactants

$$\Delta V_{cl}^0 = -RT \left[2.303pK_{AH} + \ln(p_A/q_A) - 2.303pK_{BH} - \ln(p_B/q_B) \right] - Z_{AH} + Z_{BH}$$
(16)

where pK_{AH} and pK_{BH} are the thermodynamic acidity constants of AH and BH, p_A (p_B) is the number of equivalent protons in AH (BH), q_A (q_B) is the number of equivalent basic sites in AH (BH), and Z_{AH} (Z_{BH}) is the zero-point energy of the AH (BH) bond. This procedure imposes the experimental reaction free-energy on the vibrationally-adiabatic path, and is only exact at $T=0$ K or when the entropies of the reactants and products are identical.

The zero-point energy of the reactants

$$Z_{HA} = \frac{1}{2} hc\bar{\nu}_{HA}$$
(17)

is obtained from the Morse curve of the HA bond using

$$\bar{\nu}_{HA} = \frac{1}{2\pi c} \sqrt{\frac{f_{HA}}{\mu_{HA}}} = \frac{1}{2\pi c} \sqrt{\frac{2\beta_{HA}^2 D_{e,HA}}{\mu_{HA}}} = 4.487 \times 10^{12} \frac{\beta_{HA}}{c} \sqrt{\frac{D_{e,HA}}{\mu_{HA}}} \quad (18)$$

where f_{BC} is the force constant of the BC bond, and the numerical conversion factor gives the wavenumber in cm^{-1} when the spectroscopic constant β is expressed in \AA^{-1} , the reduced mass μ_{BC} in amu, the electronic dissociation energy D_{BC} in kcal mol^{-1} , and the speed of light is $c=2.998 \times 10^{10} \text{ cm s}^{-1}$. Similar expressions give the zero-point energy of the products, Z_{HB} . These expressions ignore the very small anharmonic correction of the Morse curves for the fundamental vibrational level.

The normal modes of vibration of the linear triatomic transition state $\{A \cdots B \cdots C\}^\ddagger$ are the symmetric stretching, the antisymmetric stretching and two degenerate bendings. For a stable triatomic molecule, the symmetric and antisymmetric stretchings are calculated from Wilson's equation⁶

$$w_{\pm} = \frac{f_{ab}(\mu_A + \mu_B) + f_{bc}(\mu_C + \mu_B) \pm \sqrt{(f_{ab}\mu_A - f_{bc}\mu_C)^2 + (f_{ab} + f_{bc})^2 \mu_B^2 + 2(f_{ab} - f_{bc})(f_{ab}\mu_A - f_{bc}\mu_C)\mu_B}}{2} \quad (19)$$

where $\mu_{ij}=m_i^{-1}$, f_{ij} are the force constants of the fragments ij , and the cross terms and bendings were neglected. The solution obtained with the subtraction of the square root term, w_- is associated with the symmetric stretch, and that obtained with the addition, w_+ , with the antisymmetric stretch. The latter has an imaginary frequency and corresponds to the curvature of the classical reaction coordinate. Making $f_{ab}=f_{bc}$, we obtain

$$\mu = \frac{2}{\mu_A + 2\mu_B + \mu_C + \sqrt{(\mu_A - \mu_C)^2 + 4\mu_B^2}} \quad (20)$$

We remark that this equation has the correct limits: if all the masses are identical, then $\mu=m/3$; if A and C are much heavier than B, then $\mu=m_B/2$. The reduced mass μ is that of the antisymmetric stretch of a triatomic molecule with $D_{\infty h}$ symmetry, as expected for a linear transition state. As will be seen below, the tunneling correction employs eq (20) for the reduced mass.

The symmetric and antisymmetric stretching frequencies along the reaction path are obtained from

$$\begin{aligned} \bar{\nu}_{sym}(n) &= \frac{1}{2\pi} \sqrt{w_-} [1 - y(n)] \\ \bar{\nu}_{asym}(n) &= \frac{1}{2\pi} \sqrt{w_+} y(n) \end{aligned} \quad (21)$$

using eq (19) and the fractional force constants $f_{ij}(n)$ given by the equation of Bürgi and Dunitz⁷

$$\begin{aligned}
f_{bc}(n) &= 2D_{e,HA} (\beta_{HA})^2 (1-n)^{2a\beta_{HA}} \\
f_{ab}(n) &= 2D_{e,HB} (\beta_{HB})^2 n^{2a\beta_{HB}}
\end{aligned}
\tag{22}$$

where $a=0.26$ is Pauling's constant, and $y(n)$ is the switching function

$$\begin{aligned}
y(n) &= \cosh \left[\frac{l_{eq,BC}}{l_{eq,BC} + l_{eq,AB}} \frac{\ln(n^\ddagger)}{\ln(n/0.5)} \right]^{-1} & \text{for } n < 0.5 \\
y(n) &= 0 & \text{for } n = 0.5 \\
y(n) &= \cosh \left[\frac{l_{eq,AB}}{l_{eq,BC} + l_{eq,AB}} \frac{\ln(1-n^\ddagger)}{\ln((1-n)/0.5)} \right]^{-1} & \text{for } n > 0.5
\end{aligned}
\tag{23}$$

The switching function attenuates the frequencies to provide the correct asymptotic limits: when $n \rightarrow 0$ then $\bar{\nu}_{\text{asym}}(n) \rightarrow \bar{\nu}_{\text{HA}}$ and $\bar{\nu}_{\text{sym}}(n) \rightarrow 0$, when $n \rightarrow 0.5$ then $\bar{\nu}_{\text{asym}}(n) \rightarrow 0$ and $\bar{\nu}_{\text{sym}}(n) \rightarrow 1/2\pi \sqrt{w}$, when $n \rightarrow 1$ then $\bar{\nu}_{\text{asym}}(n) \rightarrow \bar{\nu}_{\text{HB}}$ and $\bar{\nu}_{\text{sym}}(n) \rightarrow 0$.

ISM is a unidimensional reactivity model and cannot offer a method to calculate the two degenerate bending frequencies. However, there is a good linear correlation between the symmetric stretching and bending frequencies of many triatomic systems.¹ From the slope of that empirical relation (slope = 0.43), we obtain the bending frequency from the symmetric stretching frequency. Thus, for the transition state

$$Z_{\ddagger} = \frac{1}{2} hc \left[\bar{\nu}_{\text{sym}}^{\ddagger} + 2(0.43\bar{\nu}_{\text{sym}}^{\ddagger}) \right]
\tag{24}$$

The equation above emphasizes the fact that ISM calculates the bending contribution from the symmetric stretching, and assumes a linear transition state, i.e., there are two degenerate bendings.

Now we have all the elements necessary to calculate the zero-point energy corrections along the reaction coordinate

$$Z(n) = \frac{1}{2} hc \left\{ \bar{\nu}_{\text{sym}}(n) + 2 \left[0.43\bar{\nu}_{\text{sym}}(n) \right] + \bar{\nu}_{\text{asym}}(n) \right\}
\tag{25}$$

and include them in eq (15) to obtain the vibrationally-adiabatic path.

The asymptotic limits of the stretching frequencies are closely related to those of the electrophilicity index m . In the reactants we have $m_{\text{HA}}=1$ and the Morse curve of HA is that of the spectroscopy of the isolated molecule. For the products we also have $m_{\text{HB}}=1$, for the same reasons. At the transition state, $m(n)$ attains its maximum value, given by the electrophilicity index of Parr, eq (7). Thus, we may consider that $m(n)$ varies along the reaction coordinate much in the same manner as the stretching frequencies, and calculate that variation from

$$m(n) = \frac{I_p + E_A}{I_p - E_A} [1 - y(n)] \quad (26)$$

The energy of the highest maximum along the vibrationally-adiabatic path, eq (15), minus the zero-point energy of the reactants is the vibrationally-adiabatic barrier

$$\Delta V_{ad}^\ddagger = V_{ad}^\ddagger(n) - Z_{BC} \quad (27)$$

In practice, the maximum of the vibrationally-adiabatic barrier is found numerically, using steps of $\Delta n=1/600$. The location of this maximum gives the vibrationally-adiabatic barrier, eq (27), and also the symmetric stretching frequency, eq (21). As explained above, the bending frequencies are obtained from the stretching frequencies. This barrier and the vibrational frequencies are employed in eq (4) in the calculation of the reaction rates. The only parameter still missing for such calculations is the tunneling correction.

5) Tunneling corrections

A very accurate method to calculate the tunneling correction along a unidimensional reaction path employs the semiclassical approximation.⁸ The transmission coefficient and the transmission probabilities are

$$\kappa(T) = 1 + \frac{2}{k_B T} \int_{\varepsilon_0}^{\Delta V_{ad}^\ddagger} \sinh\left(-\frac{\Delta V_{ad}^\ddagger - \varepsilon}{k_B T}\right) G(\varepsilon) d\varepsilon \quad (28)$$

$$\begin{aligned} G(\varepsilon) &= \left\{1 + \exp\left[2\gamma(\varepsilon)\right]\right\}^{-1} & \varepsilon_0 \leq \varepsilon \leq \Delta V_{ad}^\ddagger \\ &= 1 - G(2\Delta V_{ad}^\ddagger - \varepsilon) & \Delta V_{ad}^\ddagger \leq \varepsilon \leq 2\Delta V_{ad}^\ddagger - \varepsilon_0 \\ &= 1 & 2\Delta V_{ad}^\ddagger - \varepsilon_0 < \varepsilon \end{aligned} \quad (29)$$

respectively, where the barrier penetration integral is

$$\gamma(\varepsilon) = \frac{2\pi}{h} \int_{s_<}^{s_>} \sqrt{2\mu[V_{ad}(s) - \varepsilon]} ds \quad \varepsilon < \Delta V_{ad}^\ddagger \quad (30)$$

the threshold energy ε_0 is the limiting value of the vibrationally-adiabatic potential energy for exothermic or endothermic reactions

$$\varepsilon_0 = \max[V_a(s = -\infty), V_a(s = +\infty)] \quad (31)$$

the reduced mass is given by eq (20), and $s_>$ and $s_<$ are the classical turning points, i.e., the locations at which $V_a(s) = \varepsilon$.

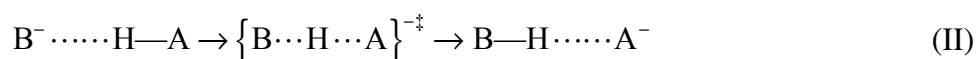
Hydrogen-atom or proton transfer transfers between heavy atoms often lead to vibrationally-

adiabatic paths with two maxima. Formally, the resolution of this problem should be made in the framework of the canonically unified theory.⁹ In practice, given the approximate nature of our treatment, it suffices to use TST with $\Delta V_{\text{ad}}^{\ddagger}$ equal to the value of the highest maximum. In these cases, the tunneling correction of the particles with energies between that of the highest maximum and the minimum between the two maxima is calculated for the highest barrier only.

It is now possible to calculate the reaction rates of the reactions illustrated in mechanism I using eq (4). Such calculations take less than a second for each temperature, using a modern computer.

6) Lippincott-Schroeder potential

The presence of a hydrogen bond along the reaction coordinate is included in the ISM reaction path using the Lippincott-Schoeder (LS) potential.¹⁰ This empirical potential relates the H-bond binding energies (D_{AB}) to the AB equilibrium distances ($l_{\text{AB,eq}}$) and to AB stretching frequency ($\bar{\nu}_{\text{AB}}$) in the $\text{B}\cdots\text{H}-\text{A}$ hydrogen-bonded complex (charges omitted)



The LS potential is expressed as a sum of four terms

$$V_{\text{LS}} = V_{\text{HA}} + V_{\text{HB}} + V_{\text{rep}} + V_{\text{el}} \quad (32)$$

where the first two terms represent covalent interactions and have the form

$$\begin{aligned} V_{\text{HA}} &= D_{\text{HA}} \left[1 - \exp(-\alpha_{\text{LS}}) \right] \\ V_{\text{HB}} &= D_{\text{H}\cdots\text{B}} \left[1 - \exp(-\beta_{\text{LS}}) \right] - D_{\text{H}\cdots\text{B}} \end{aligned} \quad (33)$$

where D_{HA} and $D_{\text{H}\cdots\text{B}}$ are the bond-dissociation energies of the unperturbed HA and H \cdots B bonds, and

$$\begin{aligned} \alpha_{\text{LS}} &= \frac{\kappa_{\text{HA}} \left(l_{\text{HA}} - l_{\text{HA,eq}} \right)^2}{2l_{\text{HA}}} \\ \beta_{\text{LS}} &= \frac{\kappa_{\text{H}\cdots\text{B}} \left(l_{\text{H}\cdots\text{B}} - l_{\text{H}\cdots\text{B,eq}} \right)^2}{2l_{\text{H}\cdots\text{B}}} \\ \kappa_{\text{HA}} &= f_{\text{HA}} l_{\text{HA,eq}} / D_{\text{HA}} \\ \kappa_{\text{H}\cdots\text{B}} &= f_{\text{H}\cdots\text{B}} l_{\text{H}\cdots\text{B,eq}} / D_{\text{H}\cdots\text{B}} \end{aligned} \quad (34)$$

In these expressions, l (or f) are the bond lengths (or the harmonic force constants) of the unperturbed HA and H \cdots B bonds. The data pertaining to the unperturbed H \cdots B bond are not usually known. Lippincott and Schroeder introduced the approximation

$$\kappa_{\text{H}\cdots\text{B}} = g\kappa_{\text{HA}} \quad (35)$$

where $g=1.45$, and showed that g is transferable to all B...H-A systems.¹¹ Additionally they assumed that

$$\begin{aligned} D_{H...B} &= D_{HA}/g \\ l_{H...B,eq} &= l_{HB} \end{aligned} \quad (36)$$

which provide all the approximations necessary to calculate the covalent contributions.

Lippincott and Schroeder expressed the repulsive term as a negative exponential and the electrostatic one as a negative power of the AB distance. Both these terms involve empirical constants. They were modified to reduce the number of constants and the following expression was obtained

$$V_{rep} + V_{el} = A \left[\exp(-bl_{AB}) + \frac{l_{AB,eq}}{2l_{AB}} \exp(-bl_{AB,eq}) \right] \quad (37)$$

The first derivative of the potential expresses the parameter A as a function of the repulsion constant b , and a set of parameters that was defined above

$$A = \frac{D_{H...B} \kappa_{H...B}}{2} \left[1 - \left(\frac{l_{H...B}}{l_{AB,eq} - l_{HA}} \right)^2 \right] \exp(-\beta) / \exp(-bl_{AB,eq}) (b - 1/2l_{AB,eq}) \quad (38)$$

The only parameter that remains to be fitted to the experimental data is the repulsion constant b . Lippincott and Schroeder chose the value $b=4.8 \text{ \AA}$. The rate constants calculated with this procedure are rather insensitive to the value of b , but the relation between the presently available bond lengths and bond strengths is better represented with $b=9 \text{ \AA}$ and this value implemented in the program.

Another important quantity in the LS potential is the force constant of the AB hydrogen bond. This can be obtained from the second derivative of the potential

$$\begin{aligned} f_{AB} &= B + A \exp(-bl_{AB,eq}) \frac{(bl_{AB,eq})^2 - 1}{(l_{AB,eq})^2} \\ B &= \frac{D_{H...B} \kappa_{H...B}}{(l_{H...B})^3} \exp(-\beta) \left[(l_{H...B,eq})^2 - \frac{\beta}{2} (l_{H...B} + l_{H...B,eq})^2 \right] \end{aligned} \quad (39)$$

The importance of this force constant lies on its relation with the AB vibrational frequency

$$\bar{\nu}_{AB} = \frac{1}{2\pi c} \sqrt{\frac{f_{AB}}{\mu_{AB}}} \quad (40)$$

The LS potential does not include a correction for the change of translational and rotational degrees of freedom on dissociation of the hydrogen bond. Such corrections are small and were neglected. However, the experimental H-binding energies, D_{AB} , are corrected for the zero-point energy of the AB vibration, Z_{AB} , to obtain the electronic binding energy of the H-bond, $D_{e,AB}$. This is done calculating $\bar{\nu}_{AB}$

from D_{AB} , to obtain a first approximation to Z_{AB} , and then recalculating the LS potential and its properties with $D_{AB}+Z_{AB}$.

7) The LS-ISM reaction path

The vibrationally-adiabatic path of ISM and the LS potential are combined to reflect the fact that a hydrogen-bonded complex brings the structure of the reactants closer to that of the transition state, as illustrated in Mechanism (II). A hydrogen bond can be regarded as an incipient proton transfer, and the bond order at the precursor complex is no longer $n=0$, but the bond order of the $B\cdots H$ bond in that complex, $n_{H\cdots B}$. Identically, for the products, the bond order is not $n=1$ but the bond order of the $H\cdots A$ bond in the successor complex, $(1-n_{H\cdots A})$. Thus, for a proton transfer in condensed media, the reaction coordinate n is only defined in the interval $[n_{H\cdots B}, (1-n_{H\cdots A})]$. The precursor and successor complexes are included in the classical reaction path of ISM with a simple transformation of the reaction coordinate¹²

$$V_{cl}(n) = (1-j)V_{HA}(1-j) + jV_{HB}(j) + k\Delta V_{cl}^0 - D_{e,AB} \quad (41)$$

where

$$\begin{aligned} j &= n - n_{H\cdots B} && \text{for } n_{H\cdots B} \leq n \leq n^\ddagger \\ j &= n - (1 - n_{H\cdots A}) && \text{for } n^\ddagger < n \leq (1 - n_{H\cdots A}) \\ k &= (n - n_{H\cdots B}) / (1 - n_{H\cdots B} - n_{H\cdots A}) && \text{for } n_{H\cdots B} \leq n \leq (1 - n_{H\cdots A}) \end{aligned} \quad (42)$$

and ΔV_{cl}^0 given by eq (16).

The LS-ISM vibrationally-adiabatic path is then calculated adding the zero-point energies along the reaction path, as indicated in eq (15), but including also Z_{AB} .

8) Rate constants for proton transfer along a H-bond

The rate of the reaction illustrated by mechanism II is the product between the concentration of the transition states at the top of the barrier $[\ddagger]=[B\cdots H\cdots A]$, and the frequency at which they pass over the barrier. Since the transition states are in thermal equilibrium with the hydrogen-bonded reactants,

$$[\ddagger] = [B\cdots H\cdots A] e^{-\Delta V_{ad}^\ddagger / RT} \quad (43)$$

and these can be related to the concentration of the separated reactants

$$K_c = \frac{[B\cdots H\cdots A]}{[B][H-A]} \quad (44)$$

this rate can be expressed as

$$k_{Hbond} = \kappa(T) \bar{\nu} K_c e^{-\Delta V_{ad}^{\ddagger}/RT} \quad (45)$$

where the tunneling correction was included as usual. In the spirit of the transition-state theory, we may assume that the reaction frequency is the “universal” transition-state frequency

$$\bar{\nu}_{TST} = \frac{k_B T}{h} \quad (46)$$

but we remark that other choices are possible. For example, the AB hydrogen bond frequency $\bar{\nu}_{AB}$ has been described as a restricted translation of the H₂O molecules along the O-H \cdots O direction,¹³ and is also a sensible choice for the reaction frequency. From weakly H-bonded systems such as H₂O \cdots HCN ($D_{0AB}=1$ kcal/mol) to strongly H-bonded systems such as H₂O \cdots HOH₂⁺ ($D_{0AB}=7$ kcal/mol), $\bar{\nu}_{AB}$ ranges from 80 to 500 cm⁻¹, and correspond to reaction frequencies between 2×10^{12} to 1.5×10^{13} s⁻¹. Eq (46) gives 6×10^{12} s⁻¹ at room temperature, which is sufficiently close to the values derived from $\bar{\nu}_{AB}$ to reassure that the model is not strongly dependent on the choice of this frequency. However, the use of the frequency $\bar{\nu}_{AB}$ has a stronger physical motivation of intramolecular systems and is employed in the corresponding rate constant calculations. Proton transfers in enzymes have the properties of intramolecular reactions and can also be calculated with the corresponding $\bar{\nu}_{AB}$ frequency.

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