

Revisiting the Arrhenius Equation in Chemical Kinetics to Analyze Kinetics Data for Photochromic Naphthoxazine-spiro-indolines

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ABSTRACT

In undergraduate courses, kinetics and thermodynamics are often taught as separate modules. It is because equilibrium data from thermodynamics do not enlighten us about the rate of attainment of equilibrium, which is kinetics. It is true that even if a chemical reaction is thermodynamically favorable, it may never happen due to kinetic considerations. However, this separation of kinetics and thermodynamics is unfortunate in some respects. In this work, the link between chemical kinetics and thermodynamics is explored based on them both being defined by a single potential energy diagram. A common misconception caused by undergraduate courses on chemical kinetics is a claim that the Arrhenius equation is deficient because it does not offer a precise meaning for the pre-exponential term A . Undergraduate courses often go on to proffer more sophisticated theories in the form of collision theory CT and transition state theory TST resulting in the Eyring equation. These latter two theories are required in order to formally show that the pre-exponential term contains information on the entropy requirements of the reaction. In this work, it will be shown that by considering the link between thermodynamics and kinetics it can easily be shown that A was already implicitly linked to the product of the entropy of activation of the reaction and the natural frequency of the reaction. This work makes use of previously published and unpublished results on photochromic naphthoxazine-spiro-indolines to compare different theories.

Keywords: Arrhenius equation, transition state theory, collision theory, naphthoxazine-spiro-indoline, photochromic, chemical kinetics

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Introduction

Photochromic naphthoxazine-spiro-indolines (NOSI) have the general photochemical and thermal reactions shown in Figure 1. (Hobley, 1995).

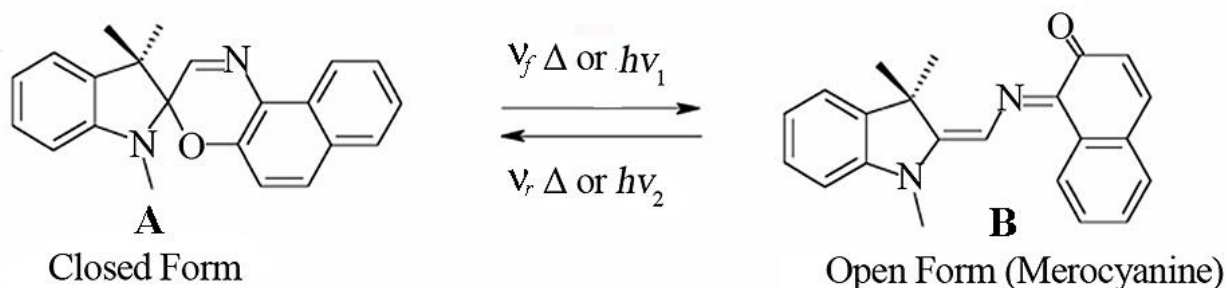


Figure 1. The NOSI photochromic reaction

where **B** is a molecular rearrangement of **A** that can be brought about photochemically or thermally in either direction of the reaction. The rate equations for the forward and reverse thermal reactions that define the thermal equilibrium are:

$$v_f = k_f[A] \text{ and } v_r = k_r[B] \quad (1)$$

where subscripts *f* and *r* denote forward and reverse reaction parameters.

Photochromic molecules of this kind are used in ophthalmic Transitions[®] lenses. In the case of Transitions[®] lenses molecule **A** is colorless and molecule **B** is coloured. In the field of ophthalmic lenses there are two very important parameters to understand. If the reaction is left alone to reach a point where the number of moles of **A** and **B** are constant (*i.e.* it has reached equilibrium), what are the constant values of the concentration of **A** and **B** relative to each other. This is important because if there is too much of colored molecule **B** in equilibrium with colorless molecule **A** at room temperature then the lens is already colored before the lens is exposed to sunlight. This parameter is covered by chemical thermodynamics. The second parameter to know is: if the reaction starts with pure **A** or pure **B** then how long does it take to convert either **A** to **B** or **B** to **A** in order to achieve equilibrium, or a quasi-equilibrium called a photostationary state (Hobley, 1995). This parameter is found from chemical kinetics.

These two fields of thermodynamics and kinetics have been studied for more than a century and are well understood based on two equations. Chemical equilibrium is described by the Van't Hoff Equation and chemical kinetics is well understood based upon the Arrhenius equation (Van't Hoff, 1887; Arrhenius, 1889). The historical background of the story of the Arrhenius equation and the Van't Hoff equation starts

with the Boltzmann distribution (Boltzmann, 1872). This distribution gives the probability of finding a component of a statistical distribution (say a molecule in the case of equilibrium of molecules) in a particular state (say state A and state B) based upon the energy gap between the two states:

$$\left(\frac{N_A}{N_B}\right) = e^{-\frac{\Delta E}{k_B T}} \quad (2)$$

where N_A and N_B are the number of species in state A or state B, respectively; $\Delta E = E_A - E_B$; E_A and E_B are the energies of states A and B, respectively; k_B is Boltzmann's constant and T is the temperature in Kelvin (Figure 2).

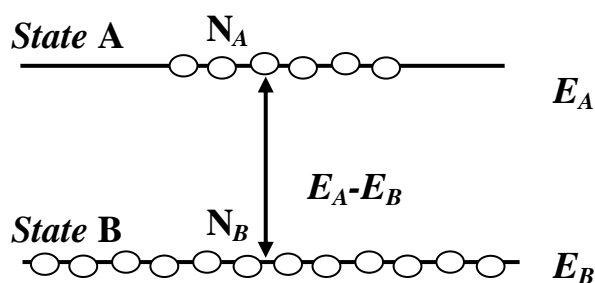


Figure 2. A Boltzmann distribution between two states with different energies

Van't Hoff took Boltzmann's distribution and applied it at the chemical equilibrium, for example where N_A and N_B are the number of molecules A and B which are linked by the chemical equilibrium.

For a simple reaction $A \leftrightarrow B$ in dynamic equilibrium as in Figures 1 and 3, the Van't Hoff equation is:

$$K_{eq} = e^{-\frac{\Delta G^o}{RT}} \quad (3)$$

where $K_{eq} = \frac{[B]}{[A]}$; $\Delta G^o = (E_A - E_B)$ and R is the universal gas constant

Since, $[B]/[A]$ is the same as N_B/N_A in the Boltzmann equation, so Van't Hoff and Boltzmann are the same expression, except that Van't Hoff is specific for chemical equilibria. The Van't Hoff equation is often written in another form as shown below:

$$\ln K_{eq} = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \text{ since } \Delta G^o = \Delta H^o - T\Delta S^o \quad (4)$$

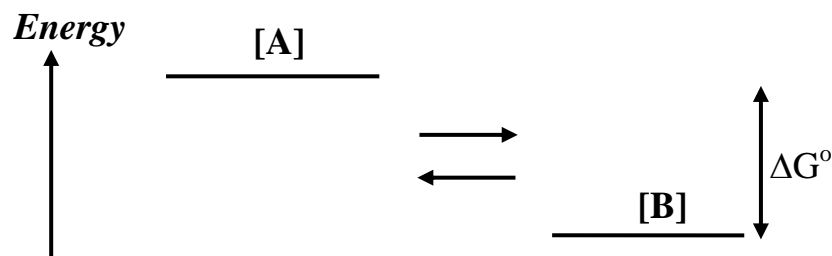


Figure 3. Energy levels for a reactant and product in chemical equilibrium.

What Arrhenius did was simply to recognise that the Van't Hoff equation assumed a dynamic chemical equilibrium. In other words, it was assumed that the chemical equilibrium is established by two competing reactions. One reaction goes one way (**A** forms from **B**) and the other reaction is the reverse of this (*i.e.* **B** forms from **A**). The rate of each reaction relative to the other determines the equilibrium. Arrhenius therefore simply postulated that the equation for each of these reactions was also governed by the same type of Boltzmann distribution. The addition was that in the energy diagram above (Figure 3), in which **A** and **B** are unconnected, there is an additional line that connects the *A* and *B* states (Figure 4).

The new line described a potential energy diagram in which activation energies are defined between states *A* and *B*. Let's say activation energy for $A \rightarrow B$ is E_{af} and the activation energy for $B \rightarrow A$ is E_{ar} .

From this description there is a new Boltzmann distribution between states *A* and *B* and the state that exists at the top of the "hill" that connects the two. The state at the top of the hill is a molecule with a conformation in between molecule **A** and molecule **B** (**AB***). In reality very fast reactions may not achieve a true Boltzmann distribution, but we will ignore this because it does not apply to this work.

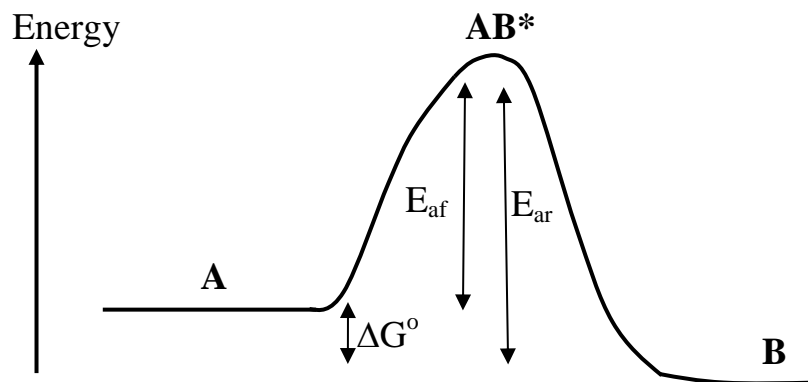


Figure 4. A potential energy diagram showing activation energies for a reversible unimolecular reaction.

Arrhenius thus proposed an empirical equation of similar form to the Van't Hoff equation. Empirical means “based on observation rather than theory or pure logic”. So, it is debatable as to whether the Arrhenius equation is purely empirical, since it was perfectly logical to propose it based on the idea that equilibrium is established by a reaction that is reversible, having a different rate for the forward and reverse reaction. The equation he proposed was:

$$k = Ae^{-\frac{E_a}{RT}}$$

(5)

where k (s^{-1}) can either be the rate constant for either A going to B or B going to A ; E_a is the activation energy (the energy gap between either state A or B and the top of the hill in between them); A is a main subject of this work and was originally known as the frequency factor (it also has units of s^{-1}), but now it is often referred to as the pre-exponential factor. This change in name is in some ways unfortunate as the title “pre-exponential factor” does not include the important point, that A is linked to the frequency at which a reaction could occur if it has enough energy.

After Arrhenius, other more sophisticated theories were proposed. The most well-known being Collision theory (CT) and Transition State Theory (TST (Trautz, 1916; Laidler and King, 1983; Atkins and De Paula, 2006)). Without fully deriving either of these theories the salient points related to this discussion will be stated.

Collision theory (CT) considered a bimolecular gas phase reaction in which molecules collide and then react if they have enough energy and if the reactive parts of the molecule are pointing the right way to react.

The rate constant is given by equation:

$$k = Z\rho e^{-\frac{E_a}{RT}} \quad (6)$$

where Z is the molar collision frequency; ρ is the steric factor; E_a is the activation energy of the reaction; T is the temperature; R is gas constant.

CT gives an equation that has the same form as the Arrhenius equation except that A is replaced by $Z\rho$, which has a steric factor ρ and a frequency factor Z . For this reason, it is generally accepted that collision theory provides a significant advance in the understanding of the pre-exponential terms compared to Arrhenius' frequency term A . However, CT does have some limitations in that it only really works in some gas phase reactions, but not in dilute solutions where most of the collisions do not result in any reaction because the collisions are with solvent molecules. Additionally, it is specific for bimolecular reactions *i.e.* it cannot be applied to the simple unimolecular reaction being considered in this work.

A further level of sophistication was added by another well-known theory, Transition State Theory (TST), which again starts with a potential energy surface, but this time it is a surface specifically in ΔG°

(Figure 5) for a reaction of the form:



for which the following equations apply:

$$K^* = \frac{[AB^*]}{[A]} \quad (7)$$

i.e. an equilibrium is assumed between the reactant **A** and the transition state **AB*** with an equilibrium constant K^* .

$$[AB^*] = K^*[A]$$

$$\frac{d[B]}{dt} = k^*[AB^*] \text{ is the rate of formation of } \mathbf{B} \text{ from } \mathbf{AB}^*$$

$$\frac{d[B]}{dt} = K^*k^*[A]$$

where k^* is the breakdown rate constant of **AB***. and $k^* = \kappa\nu$; κ is the fractional efficiency with which the bond in **AB*** breaks to form **B** and is assumed to be 1; ν is the **AB*** breakdown frequency (assumed to be the timescale of one bond vibration or k_bT/h).

$$\text{If } k = K^*k^* \text{ then } k = K^* \frac{k_bT}{h}$$

But just like in thermodynamics equations 3 and 4 it can be written:

$$\ln K^* = \frac{\Delta H^*}{RT} - \frac{T\Delta S^*}{R}$$

so finally, the Eyring equation can be written:

$$k = \left(\frac{k_bT}{h}\right) e^{\frac{\Delta S^*}{R}} e^{-\frac{\Delta H}{RT}} \quad (8)$$

In TST, just like in CT, there is a frequency term (compare Z with k_bT/h) and a steric term (compare ρ with $e^{\Delta S^*/R}$) but this time the steric term is directly associated with a reaction entropy.

However, some assumptions were also made in TST and thus some flexibility on how to interpret the results obtained using this equation is lost. For example, it was assumed that 100% of **AB*** forms **B** (it was assumed the transmission coefficient $\kappa=1$). But that is not necessarily the case. It was also assumed that the breakdown frequency of **AB***, ν , is equal to a bond vibration frequency (k_bT/h) which could well be true for a bimolecular reaction or a dissociation, but in some reactions like an isomerization the timescale for a bond rotation may be more appropriate and the assumption that $\kappa=1$ is probably not valid. In summary CT and TST give a more rigorous insight as to the meaning of the pre-exponential term, but at the cost of flexibility, in terms of the general applicability of the models.

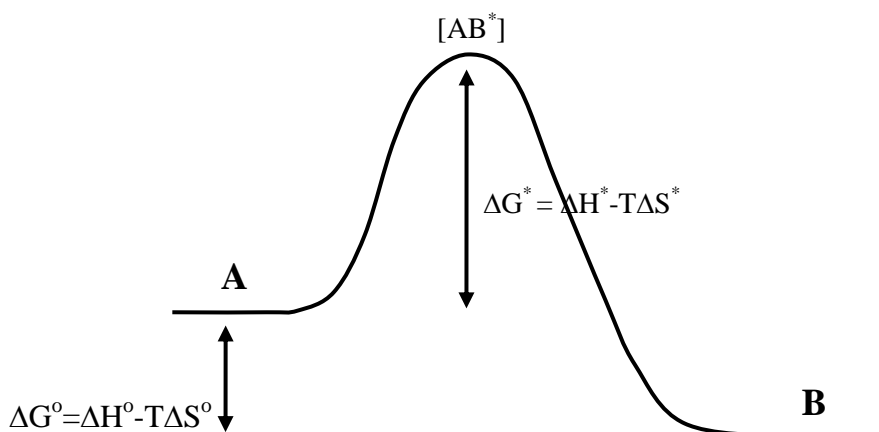


Figure 5. A potential energy surface in Gibbs free energy corresponding to the derivation of the Eyring equation in TST in which the reaction is not reversible.

Interpretation of the Arrhenius equation based upon a reversible equilibrium

From thermodynamics for a simple reaction $A \leftrightarrow B$ in dynamic equilibrium, the equilibrium constant is the fractional ratio of the respective concentrations of the products over the reactants (equation 3). Furthermore, it can be shown that K_{eq} is related to the ratio of the rate constants of the forward and reverse reactions (equation 1) because at equilibrium the forward reaction rate = the reverse reaction rate *i.e.*:

$$k_f[A] = k_r[B] \quad (9)$$

$$\frac{k_f}{k_r} = \frac{[B]}{[A]} = K_{eq}$$

Previously two potential energy diagrams were presented in Figures 4 and 5. One used ΔG^* for the activation energy and the other used E_a but how does E_a relate to ΔG ? Also how does A relate to any thermodynamic properties? This will be addressed next.

The Arrhenius equation (equation 5) can be written for the forward and reverse reaction:

$$k_f = A_f e^{-\frac{E_{af}}{RT}} \text{ and } k_r = A_r e^{-\frac{E_{ar}}{RT}} \quad (10)$$

Inserting these into equation 8:

$$K_{eq} = \frac{k_f}{k_r} = \frac{A_f e^{-\frac{E_{af}}{RT}}}{A_r e^{-\frac{E_{ar}}{RT}}} \quad (11)$$

$$K_{eq} = \left(\frac{A_f}{A_r}\right) e^{-\frac{E_{ar}}{RT}} e^{-\frac{E_{af}}{RT}}$$

but from thermodynamics equations 3 and 4 it will be:

$$\ln K_{eq} = \ln A_f - \ln A_r - E_{af}/RT + E_{ar}/RT = -\Delta G^{\circ}/RT = -\Delta H^{\circ}/RT + \Delta S^{\circ}/R$$

$$-\ln K_{eq} = -\ln A_f + \ln A_r + E_{af}/RT - E_{ar}/RT = \Delta G^{\circ}/RT$$

$$\Delta G^{\circ} = (E_{af} - E_{ar}) - RT \ln A_f + RT \ln A_r$$

$$\Delta G^{\circ} = (E_{af} - E_{ar}) - T(R \ln A_f - R \ln A_r) \quad (12)$$

Comparing this with equation 4:

$$\Delta H^{\circ} = (E_{af} - E_{ar}) \quad (13)$$

$$\Delta S^{\circ} = R(\ln A_f - \ln A_r)$$

$$k_b = R/N_A$$

$$\Delta S^{\circ} = k_b N_A (\ln A_f - \ln A_r) \text{ per mole} \quad (14)$$

$$\Delta S^{\circ} = (k_b \ln A_f - k_b \ln A_r) \text{ per molecule}$$

Compare this equation with Boltzmann's entropy equation (Boltzmann, 1896; Boltzmann, 1898) from statistical thermodynamics:

$$S = k_b \ln W \quad (15)$$

where W is the number of microstates corresponding to a given macrostate.

Hence it is reasonable to suggest that A , the pre-exponential term, is very much intrinsically an entropy term and is itself a number related to several microstates in the system that are "specific to making the reaction work". A is most likely the probability of occurrence of the exact microstates that can exist in the system that put the molecules in the reaction in exactly the right place at the right time to react. It must contain a logarithmic term as we derived, but it has units of s^{-1} so it must also contain a frequency term that is the natural frequency of the transformation taking place, just as for CT. In CT the pre-exponential term A was replaced with ρZ where ρ is a steric term, which is implicitly therefore an entropy term, and Z is a collision frequency. Z has a very specific definition based upon kinetic theory of gases and many body theories and is largely determined by gas phase diffusion. With TST and the Eyring equation A is replaced with $(k_b T/h) e^{\Delta S_f^*/R}$. In this case the entropy term is $e^{\Delta S_f^*/R}$ and the frequency term is $k_b T/h$. The Arrhenius A term frequency component would also involve a transmission probability κ , as in TST, but in the case of an isomerization like the NOSI system is likely to be ~ 0.5 , because at the top of the hill both forward and reverse reactions would have nearly equal probability.

In summary, although by inserting the Arrhenius equation into thermodynamics, we have not derived absolute values of activated parameters, it has been shown that A is associated the reaction

activation entropy and E_a is associated with the activation enthalpy, *i.e.* $\Delta H^\circ = (E_{af} - E_{ar})$ and $\Delta S^\circ = R(\ln A_f - \ln A_r)$.

Moreover $\Delta S^\circ = (k_b \ln A_f - k_b \ln A_r)$ which can be compared with Boltzmann's entropy $S = k_b \ln W$.

It suggests that the ratio of A_f/A_r and W_f/W_r for forward and reverse reactions are equivalent, noting that any non-entropy related frequency terms must have cancelled out. Admittedly Arrhenius published his equation in 1889 whereas Boltzmann's entropy from statistical thermodynamics was published ~10 years later, in 1898. Note in this timeline that Trautz published his collision theory 1916 and TST was published in the 1930. So, Arrhenius may not have recognized the link between A and Boltzmann's entropy. However, since Arrhenius was one of Boltzmann's students that is highly unlikely.

What does each part of the Arrhenius equation say and how are they useful for understanding of kinetics? The units of a first order k are s^{-1} and the units of A also s^{-1} so both are frequencies, but they are not the same frequency of course. k is smaller by a factor $e^{-E_a/RT}$, so in order to make them equal, A is multiplied by $e^{-E_a/RT}$ and this is the first important thing. It is obvious mathematics, but it is important to note, because k is the frequency at which molecules react in a given reaction. That is what a first order rate constant is, just a reaction frequency. So, what does the other side of the equation say? A is a lot bigger than k , and it is the probability of molecules in our unimolecular reaction presenting themselves in the correct place and in the correct shape and orientation to react, combined with the limiting rate (frequency) at which they can rotate, break or otherwise modify their chemical bonds.

Now if all molecules bumping into each other (making sure they are the right kind and pointing the right way) reacted then $A = k$, but it is not that easy for molecules to react. Normally for a reaction to occur a molecule must be pulled apart, a bond must break, or a few electrons must move *etc.* and although it may be assumed that it is going to get more stable eventually, it must be realized that there is a bit pain before the gain and it is necessary to give a little energy to get the reaction started. That energy is E_a on the potential energy diagram. The reactant molecules must have energy equal to E_a in order to get over the hill on the potential energy diagram in order to get to the other side and become a product. But where do they take it from? Well, they can only take it from the thermal reservoir which is $k_b T$. A single molecule gets E_a from $k_b T$ and a mole of molecules gets E_a from RT because RT has 6.02×10^{23} times more energy.

At room temperature $k_b T = 4.11 \times 10^{-21}$ J and $RT = 2479$ J mol⁻¹. That amount of energy does not seem to be very much, because E_a is normally many times bigger, usually ~several kJ mol⁻¹. So, it may seem that it is difficult to get the molecule up the activation hill. However, $k_b T$ is an average energy, so sometimes there is more energy and sometimes less. In fact, the molecule just waits for more energy to arrive. Boltzmann's distribution dictates how many molecules have enough energy at a given time, or, in

other words, how often a molecule possess E_a at a given temperature.

But how often it will happen that a molecule possesses E_a ? Well, on average the molecules don't have enough energy, but they do $e^{\frac{-E_a}{RT}}$ of the time. Let's put numbers in. E_a could reasonably be 50000 J mol⁻¹ so $e^{-(50000)/(2479)}$ of the time the molecules have sufficient energy and the reaction happens if they satisfy the entropy requirements from A . That's 1.7×10^{-9} of the time. So, this reaction could take some time! But, don't give up yet because A can easily be $>10^{11}$ s⁻¹. That's why A must be a lot bigger than k , for a reaction to occur in reasonable time, because Boltzmann's distribution only gives us energy equivalent to E_a for a tiny fraction of the time, and the rest of the time the energy is too low. So, the meaning of the equation can be broken down into its component parts. k is the number of times the reaction happens per second. A is the total number of times the molecule is positioned in the right way to react, coupled with the frequency at which the process naturally occurs, *e.g.* bond breaking, rotating, forming, *etc.* $e^{\frac{-E_a}{RT}}$ is the fraction of the time that the Boltzmann distribution gives the molecule enough energy to make the reaction happen. Next, the Arrhenius equation will be used with some published and unpublished data from previous works, assuming that the pre-exponential term is a composite of a frequency term and an entropy term (Hobley, 1995; Hobley and Wilkinson, 1996; Hobley et al., 2003; Wilkinson and Hobley, 1992; Wilkinson et al., 1996).

Experimental

All experimental procedures are already published and freely available on-line (Hobley, 1995). In the interests of brevity, they will not be repeated here.

Results and Discussion

Naphthoxazine-spiro-indolines (NOSI) are compounds from the general class of spiro-oxazine. They are best known for their use in Transitions^(TM) ophthalmic photochromic lenses. The photochemical reaction occurs in a few picoseconds. The thermal fade reaction occurs in seconds to minutes (Hobley, 1995; Hobley and Wilkinson, 1996; Hobley et al., 2003; Wilkinson and Hobley, 1992; Wilkinson et al., 1996). These are compounds that can switch from a colorless form to a coloured form in chemical reactions induced by heat or light. The generic reaction scheme is shown in Figures 1 and 6.

A homologous series of such molecules (Figure 7) that are identical except length of an alkyl chain on the indoline nitrogen, was studied for this work. The alkyl chain modification was done with the

intention of hindering thermally induced ring closure. As can be seen from the first order rate constants for the thermal fade reaction from the colored **B** merocyanine to the colorless **A** spiro-form, shown in Table 1, this strategy worked.

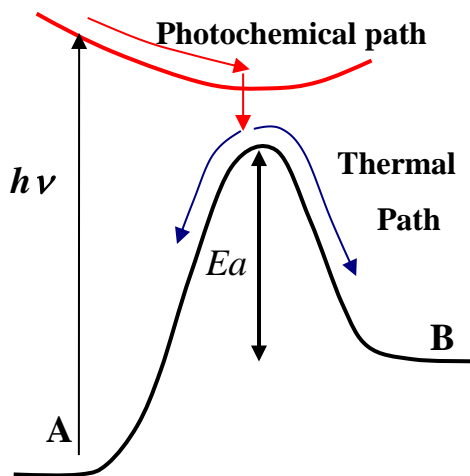


Figure 6. The ground state and excited state potential energy surface for a NOSI compound.

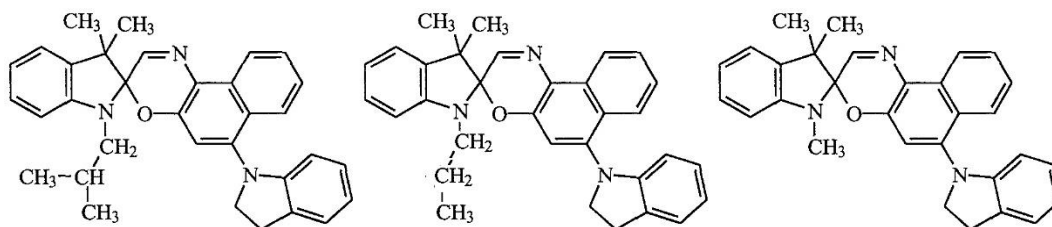


Figure 7. The homologous series of NOSI molecules studied

The first order rate constants for this thermal ring closure reaction of these three compounds were determined as a function of temperature and typical plots using the Eyring equation and the Arrhenius equations were made (Figure 8). The typical Eyring equation plot is $\ln(k/T)$ against $1/T$ to obtain a straight line with a slope of $\Delta H^*/R$ and an intercept of $\ln(k/h) + \Delta S^*/R$. The Arrhenius plot of $\ln k$ against $1/T$ yields a straight line with a slope of E_a and an intercept of A . The extracted data is summarized in Table 1. As can be seen in Table 1, there is no significant difference in ΔH^* derived from the Eyring equation or from the Arrhenius plots for the different compounds studied. These values can be considered to be reliable, because they are not affected by assumptions in either treatment. Thus, it can be concluded that the effect of the alkyl chain length does not affect the value of ΔH^* and the source of the slowing of the thermal ring closure reaction with increasing chain length must be due to something else.

Not surprisingly since both Eyring and Arrhenius treatments yield three parallel straight lines and it

is the intercepts that are the big difference in each case. In other words, the differences are in the entropy terms, if there are no changes in the frequency components. This assumption is reasonable since the same kind of intramolecular rearrangement occurs in all three cases. This assumption is always made for Eyring as $\kappa\nu$ is assumed to be k_bT/h , and the three intercepts therefore contain the same $\ln k_b/h$ term.

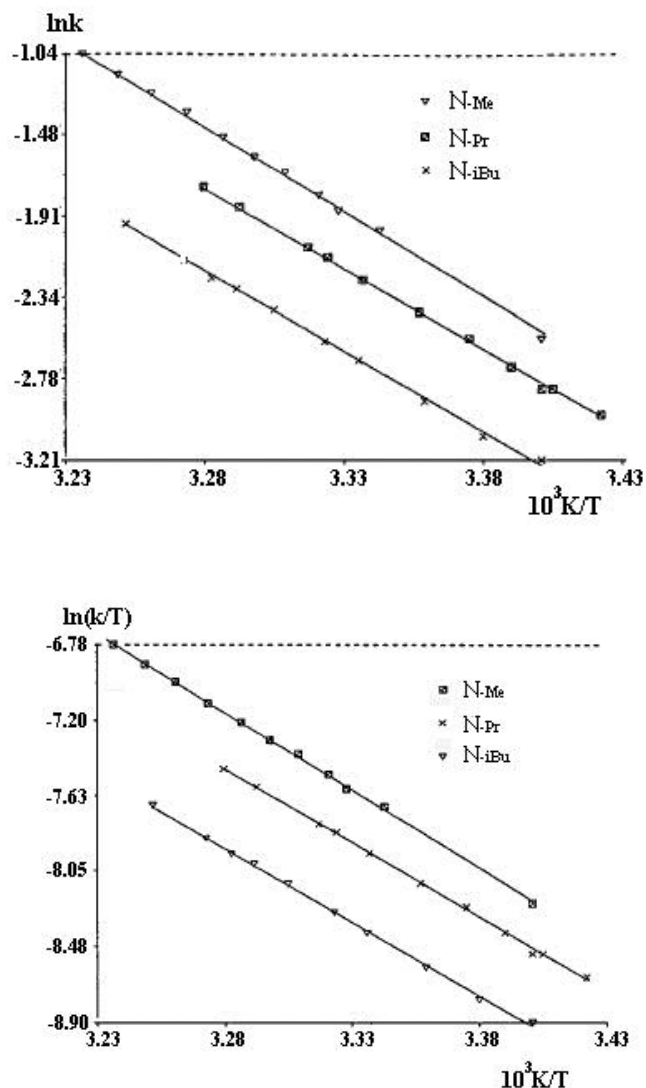


Figure 8. Arrhenius and Eyring plots for the thermal ring closure reaction of the homologous series of NOSI compounds (Hobley, 1995)

In the case of Arrhenius, the same assumption can be made based on reasoned arguments as to why it is valid or why it is invalid. In this case it is probably invalid to use the Eyring assumption. The Eyring equation gives “comforting” values of ΔS^* , however, this is because a value for $\kappa\nu$ was assumed, which

may not be valid for the following reasons. The ring closure reaction is not the same as the description of the transition state of TST in which the activated transition state dissociates within one vibration. In the ring closure reaction, nothing is dissociating. The molecule is twisting around a central single bond on the methine bridge. Arguably the use of the breakdown frequency $k_b T/h$ for ν is incorrect because no bonds need to break at all in this twisting isomerisation. Furthermore, the transmission efficiency factor, κ , is not likely to be 1, because once the twisting molecule gets halfway through its motion, it could easily either reform the starting ring open form or continue to the ring closed form.

Table 1. Kinetic parameters for the homologous series of naphthoxazine-spiro-indolines in toluene

N_{alkyl}	$E_a^{1(B \rightarrow A)}$ kJ mol^{-1}	$\Delta H_{(B \rightarrow A)}^{*2}$ kJ mol^{-1}	Intercept ¹	A^1 s^{-1}	$(\Delta S^*)^2$ $\text{J K}^{-1} \text{mol}^{-1}$	$e^{-\Delta H^*/RT}$ 298 K	$k_{294 \text{ K}}$ s^{-1}
$N_{\text{-Me}}$	73.2	70.6	27.87	1.3×10^{12}	-16.6	6.3×10^{-14}	0.077
$N_{\text{-Pr}}$	71.8	69.6	25.69	1.8×10^{11}	-32.8	4.3×10^{-13}	0.059
$N_{\text{-iBu}}$	71.6	69.0	25.90	1.5×10^{11}	-37.6	2.2×10^{-13}	0.040

¹from Arrhenius equation; ² from Eyring equation

The Eyring derived values of ΔS^* can safely be taken as relative values. However, less credence should be given to the actual values.

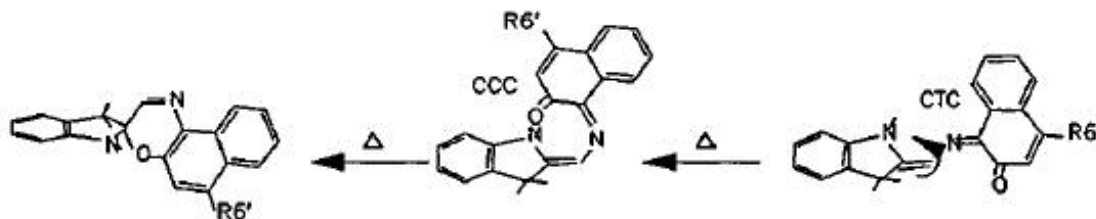


Figure 9. The proposed mechanism for the thermal ring closure reaction.

What we can say is that the ring closure reaction should go through the conformation which is *cis-cis-cis* CCC about the central methine bridge (Figure 9), because it is apparent that the $N_{\text{-alkyl}}$ groups are hindering the reaction. The naphthalene moiety will collide with larger $N_{\text{-alkyl}}$ chains only if it passes through the CCC form. Furthermore we can state that it is probably the activation entropy of the reaction, ΔS^* , that is slowing down the reaction for larger $N_{\text{-alkyl}}$ groups, since the larger $N_{\text{-alkyl}}$ groups have to move out of the way, meaning that the molecule must adopt a specific conformation before the ring closure can be completed. However, we clearly cannot trust the absolute entropy values.

In comparison, the diminishing values of A with increasing N_{alkyl} bulkiness also allows us to infer that entropy is the key factor here because we have already argued that A is a combined frequency and activation entropy term. From A we can determine the frequency of the reaction if the process was occurring in the absence of an activation energy. In changing from N_{Me} to N_{Pr} to N_{iBu} the reaction frequency changes from $1.3 \times 10^{12} \text{ s}^{-1}$ (0.8 ps) to $1.8 \times 10^{11} \text{ s}^{-1}$ (5.6 ps) to $1.5 \times 10^{11} \text{ s}^{-1}$ (6.7 ps). For reference the frequency factor in TST ($k_b T/h$) has a room temperature value of $6.3 \times 10^{12} \text{ s}^{-1}$ meaning that the reaction is expected to occur in 150 fs in the absence of other hindering factors. The ring closure reactions of NOSI compounds are between 5 to 40 times slower than that. Since this is a simple reaction in which nothing dissociates, no bonds need to break and only a simple torsion around the central single bond on the methine bridge is required. It could justifiably be suggested that the reaction activation entropy for the N_{Me} compound is close to zero, because the N_{Me} group cannot hinder the reaction and it cannot change its conformation relative to the naphthalene moiety during the reaction. Thus, it can be suggested that a realistic natural frequency for this type of reaction is equal to the value of A obtained from the Arrhenius plot intercept for the N_{Me} compound ($1.3 \times 10^{12} \text{ s}^{-1}$) and that the reaction should proceed on the sub-picosecond timescale (0.8 ps) if a molecule possess E_a . In other words, by assuming nothing until the end. We could extract a candidate number for the frequency component of A by reasonably assuming that the activation entropy is negligible (an assumption stated is one that can later be refuted).

Using this information it can further be suggested that a reasonable candidate values of actual activation entropies for the N_{Pr} and N_{iBu} compounds by assuming there is low to no entropy term for the N_{Me} compound and assuming very reasonably that the entropy term in A is of the form $F e^{\Delta S^*/R}$. It can just be assumed that a good value for the natural reaction frequency (F) is the same as for the N_{Me} molecule (1.3×10^{12}).

In the case of the N_{Pr} compound $A = 1.8 \times 10^{11} = 1.3 \times 10^{12} e^{\Delta S^*/R}$ from which $\Delta S_{N-\text{Pr}}^* = -16.4 \text{ J K}^{-1} \text{ mol}^{-1}$ can be calculated. Similarly, $\Delta S_{N-\text{iBu}}^* = -17.9 \text{ J K}^{-1} \text{ mol}^{-1}$ can be determined.

It can be seen from the first order rate constants for the thermal fade reaction from the colored **B** merocyanine to the colorless **A** spiro-form, shown in Table 1, were successfully slowed down by a bulkier N_{alkyl} group. But moreover, we can quantify this in terms of the activation entropy of the reaction. To achieve this, it has simply been proposed, based on equation (13) CT and TST, that the Arrhenius A – term has a form $(F_A^{B \rightarrow A}) e^{\Delta S^*/R}$ where $(F_A^{B \rightarrow A})$ is the frequency component of the A term. However, unlike for CT and TST it was not necessary to fix a value for the frequency component or assume any breakdown efficiency that is not based on a knowledge of the system under investigation.

Comparison with NOSI photochemistry

As can be seen in Figure 6, in photochemistry it is possible to jump the molecule into an excited state using a photon's energy. In this excited state, the molecule may react with zero activation energy to form products. Thus, it is possible to compare the derived thermal-reaction frequencies with real values measured in the absence of any E_a . These photochemical reactions happen very fast. It is known from data from picosecond pump-probe experiments that in non-polar cyclohexane the N_{iBu} compound photoisomerizes with a rise-time $\tau_{rise} \sim 5$ ps (Table 2) (Hobley, 1995; Hobley and Wilkinson, 1996; Hobley et al., 2003; Wilkinson and Hobley, 1992; Wilkinson et al., 1996). This means A in the direction $A \rightarrow B$ is $2 \times 10^{11} \text{ s}^{-1}$ (5 ps) because in photochemistry light is used to jump straight to the top of the hill and there is no activation enthalpy term (no E_a). It compares rather well with the $(F_{\Delta}^{B \rightarrow A}) e^{\Delta S^{\ddagger}/R} \sim 1.5 \times 10^{11} \text{ s}^{-1}$ (6.7 ps) for the same compound in toluene in the thermally activated reaction. The rate of the reaction is just a little slower in the ground state. However, in the case of photochemistry, for compounds with N_{Me} and N_{iBu} groups in non-polar solvents the quantum efficiency (number of molecules reacted/number of photons absorbed) $\phi_{A \rightarrow B}$ is high and it is not altered by the N_{alkyl} chain length (Table 2). Furthermore, between cyclohexane and toluene there is no significant difference in the quantum efficiencies of the ring-opening reaction. In other words, the trend observed for the thermal fade reaction in which the methine bridge rotation is hindered in the order $N_{iBu} > N_{Pr} > N_{Me}$; it is not seen when comparing photochemical quantum efficiencies, for which there is no N_{alkyl} effect. It is thus proposed that the photochemical reaction does not go through the same CCC intermediate as in the thermal reaction, because in that conformation steric factors should reduce the reaction efficiency for the compounds with longer bulky chains as in the ground state. Therefore, the proposed intermediate in the photochemically induced rotation is the *trans-cis-cis* TCC form in which the naphthalene moiety cannot bump into the N_{alkyl} chains.

Comparing the reverse Arrhenius frequencies (Table 1) with the forward photochemical frequencies in non-polar solvents (Table 2) shows that the reaction frequency of the photochemical forward reaction and the thermal reverse reaction is very similar except that the thermal reaction is a little slower. Let's assume that the photochemical reaction frequency is of the same form as the A term in Arrhenius, *i.e.* it is possible to write it as a combination of an entropy term and a frequency term, for example:

$$(F_{\Delta}^{B \rightarrow A}) e^{\Delta S^{\ddagger}/R} \sim 1.8 \times 10^{11} \text{ s}^{-1} \text{ (6.6 ps)} N_{iBu} \text{ in toluene}$$

$$(F_{\Delta}^{A \rightarrow B}) e^{\Delta S^{\ddagger}/R} \sim 2 \times 10^{11} \text{ s}^{-1} \text{ (5.0 ps)} N_{iBu} \text{ in cyclohexane}$$

The high quantum yield for $\phi_{A \rightarrow B}$ in non-polar solvents implies that, all things taken into account, the progression from the S_1 state of the spiro-form to the ground state of the mero-form is highly favored by efficient internal conversion between S_1 and S_0 and upon dropping down to the ground state surface; in

non-polar solvents the molecules favor ring-opening more than ring-closure. It means that the transmission factor κ in the frequency term is >0.5 , probably because the molecule does not drop onto the top of the hill in the ground state potential energy surface, but rather drops down on the B-side of the hill.

Table 2. Photochemical parameters (Hobley, 1995; Hobley and Wilkinson, 1996; Hobley et al., 2003; Wilkinson and Hobley, 1992; Wilkinson et al., 1996)

Compound	Solvent	τ_1 / ps (k_1)	τ_2 / ps (k_2)	$\phi_{A \rightarrow B}$
N _{-Me}	BuOH	7.1 (1.4x10 ¹¹)	790 (1.3x10 ⁹)	0.22
N _{-iBu}	PrOH	7.1 (1.4x10 ¹¹)	560 (1.8x10 ⁹)	
N _{-iBu}	BuOH	7.1 (1.4x10 ¹¹)	790 (1.3x10 ⁹)	
N _{-iBu}	DeOH	7.1 (1.4x10 ¹¹)	1100 (9.1x10 ⁸)	
N _{-iBu}	CHX	5.0 (2.0x10 ¹¹)	Over in τ_1	0.70
N _{-Me}	CHX			0.72
N _{-iBu}	Toluene			0.67
N _{-Me}	Toluene			0.64

Note that on the excited state the potential energy surface the molecule undergoes charge separation in which electrons from the oxazine oxygen and the spiro carbon delocalize to the indoline nitrogen as the oxazine oxygen takes on a phenolic character (Figure 10) with the TCC conformation. This is a zwitterionic intermediate in which the central bond on the methine bridge is double bonded. This double bond character should hinder rotation. However, if the molecule drops down onto the ground state surface the phenolic oxygen should transfer its negative charge back to the positive indoline nitrogen to form a non-charge separated TCC quinoidal form in which the central methine bridge bond is a single bond. In this conformation a single rotation about the single bond would easily form a merocyanine with TTC form. The lifetime of the charge separated zwitterionic state should be shorter in non-polar solvents and could be longer in polar solvents such as alcohols, because these could help to solvate the charge separated state. Indeed, from Table 2, in polar solvents (alcohols) there is a much longer lived transient in the photochemical isomerization after the rapid (7 ps) formation of an intermediate state.

The formation of the fast transient is independent of solvent viscosity and corresponds to $(F_A^{A \rightarrow B}) e^{\Delta S^*/R} \sim 1.4 \times 10^{11} \text{ s}^{-1}$. Furthermore, it does not change with the N_{-alkyl} chain length. This transient must be formed with only slight changes in the molecular shape. This timescale can be attributed to the formation of the charge separated zwitterionic cisoid TCC merocyanine isomer. The longer lived transient state absorbs broadly across the visible (Hobley et al., 2003) and has an $(F_A^{A \rightarrow B}) e^{\Delta S^*/R} = 1.8 \times 10^9$ (560 ps) 1.3×10^9 (790 ps) – 9.1×10^8 (1100 ps) in propanol, butanol, and decanol, respectively. Its lifetime is affected by viscosity but is independent of the N_{-alkyl} chain length. In other words it should involve significant molecular rotation

because it is affected by solvent viscosity, but it must rotate in a way such that the N_{-alkyl} chain cannot clash with the naphthalene moiety during the transformation, *i.e.* it should go through the ground state quinoidal TCC isomer. The longer lifetime, of hundreds of picoseconds, supports the transient being charge separated, *i.e.* the molecule is in its zwitterionic form in which bond rotation is hindered. This should drop down onto the ground state surface to form the TTC quinoidal merocyanine, but the hold up on the excited state should increase the chance of internal conversion and vibrational cascade, thereby lowering the quantum efficiency of the photochemical transformation from **A** to **B** (as seen in Table 2 for the polar solvent quantum efficiency). Hence, a full mechanism for the photochemical ring opening and thermal ring closure can be proposed that fits all the kinetic and photochemical data in Tables 1 and 2. This is shown in Figure 10.

From the transient absorption spectra (Hobley et al., 2003) obtained in butanol it may also be reasonably suggested that the broad absorption across the visible for the transient assigned to a zwitterionic TCC molecule on the S₁ surface implies that this transient is indeed in its excited state for which the energy gap S₁→S₂ would be smaller than transitions from ground states and because such broad featureless spectra extending to long wavelength are typical for the lower energy S₁→S₂ transition (Tamai and Masuhara, 1992).

When suggesting that a transient on the S₁ surface is stabilized compared to the transient on the S₀ surface (S₁v₀ is far higher in energy than S₀v₀) it must be remembered how internal conversion occurs. Internal conversion does not have an activation barrier, *i.e.* E_a is zero. E_a is heavily associated with ΔH* meaning that internal conversion must be dominated by ΔS*. This is actually obvious when it is considered that internal conversion involves the electronically excited, yet vibrationally and rotationally “cold” S₁v₀ state converting into a state equal in energy (iso-energetic) that exists on the ground state surface, which is the vibrationally “hot” S₀v_n state (subscript *n* indicates the *n*th vibrational level of S₁ that energetically matches S₀v_n). The parameter that holds up this conversion does not involve enthalpy so much, but it is dominated by entropy. Internal conversion obeys the Franck-Condon principle (Condon, 1926; Franck, 1926). That means that for an electronic transition to happen the Born-Oppenheimer approximation must apply (Born, 1927). Born-Oppenheimer suggests that there is a zero nuclear motion during an electronic transition. It means that for internal conversion to happen the molecule must, more-or-less inter-atomically map onto the state that it is about to become. If the excited state is polar and solvated in a polar solvent, it is less likely to map, atom-to-atom onto a non-polar ground state that is less solvated in the polar solvent. Thus, the hold-up for the photo-isomerization in the alcohols is also apparently due to the entropy term in the reaction frequency of the transformation ((F_Δ^{A→B}) e^{ΔS*/R}). The natural frequency of the reaction should be like the natural frequency on the ground state because it is still a nearly identical rotation about a single bond. It is

then possible to produce a plausible number for the entropy term for the internal conversion in alcohols (ignoring possible differences in κ).

Previously it was proposed that $F_{\Delta}^{B \rightarrow A}$ for the N_{Me} is 1.3×10^{12} and this number can be used to try to separate the proposed frequency component and entropy terms. We know that $(F_{\Delta}^{A \rightarrow B}) e^{\Delta S^*/R}$ is 1.8×10^9 (560 ps), 1.3×10^9 (790 ps) and 9.1×10^8 (1100 ps) in propanol, butanol, and decanol, respectively. For the N_{iBu} reaction in propanol we can write

$$1.8 \times 10^9 = 1.3 \times 10^{12} e^{\Delta S^*/R}$$

$e^{\Delta S^*/R} = 1.8 \times 10^9 / 1.3 \times 10^{12} = 1.38 \times 10^{-3}$ if the frequency term for the N_{Me} compound applies to the N_{iBu} compound, which is reasonable, because the N_{Me} substitution has been shown to affect the reaction entropy. From this we can calculate that $\Delta S^*/R = -6.6$. This means that $\Delta S^* = -55 \text{ J mol}^{-1} \text{ K}^{-1}$ in propanol. Similarly, $\Delta S^* = -57 \text{ J mol}^{-1} \text{ K}^{-1}$ in butanol and $-60 \text{ J mol}^{-1} \text{ K}^{-1}$ in decanol can be calculated. The differences between these three solvents is no doubt due to additional entropy contributions due to solvent viscosity. In other words, the solvent molecules must move out of the way of the rotating moieties.

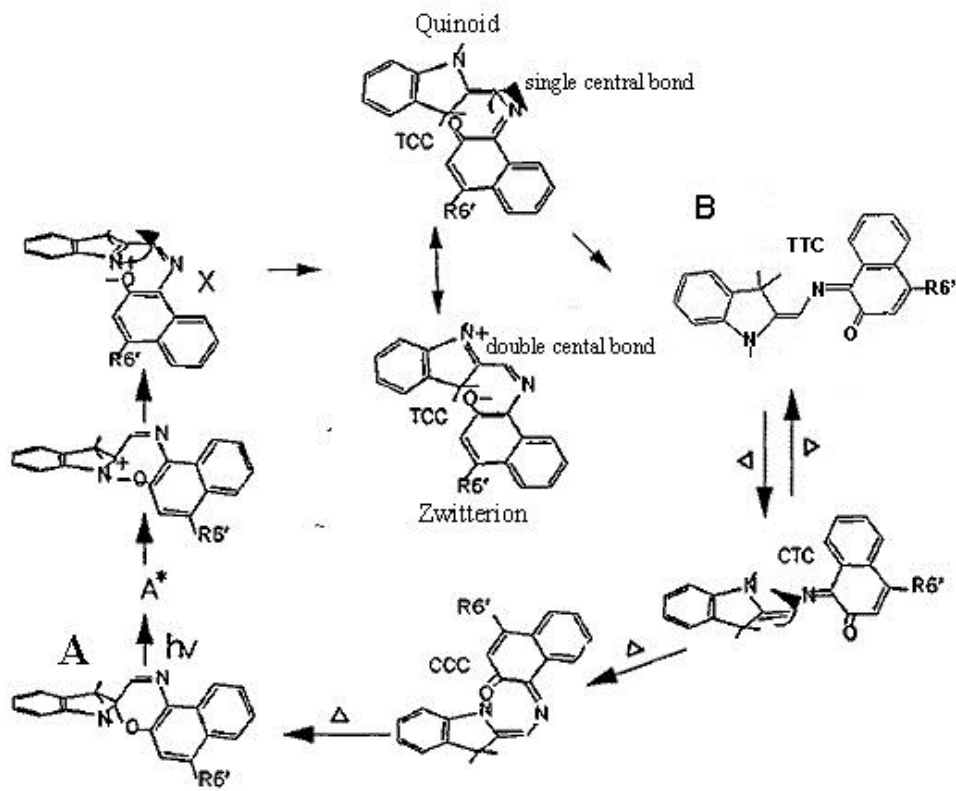


Figure 10. The proposed full photochemical and thermal reaction mechanism for a NOSI compound

Conclusion

It has been demonstrated that the simple application of the Arrhenius equation using assumptions specific to the molecular system under investigation can yield values of E_a and A . Since A can safely be assumed to be a composite of an entropy and an enthalpy term *i.e.* $A=(F_{\Delta}^{B\rightarrow A}) e^{\Delta S^*/R}$, it means that in some cases the terms $(F_{\Delta}^{B\rightarrow A})$ and ΔS^* can be separated when the entropy or frequency term can be reasonably assumed to have a known probable value. Using this approach, thermal reaction and photochemical reactions of naphthoxazine-spiro-indolines have been compared. By doing so, it has been possible to propose a full reaction scheme for the entire photochromic reaction of these commercially important molecules. The Arrhenius A reaction frequency for the ground state was almost the same as the frequency of the first order rate constants for the photochemical reaction in non-polar solvents. However, the photochemical frequencies obtained in polar solvents was significantly slower than in non-polar solvents. It is suggested that this is because the molecule gets held up as a zwitterionic excited state for which the bond rotation to form the ring open merocyanine is hindered by a double central bond on the methine bridge. The molecule must drop to S_0 before it can isomerize. Hence when extracting reaction frequency terms, care must be taken to understand the type of molecular process that is being studied. Some reactions are naturally slower than others by virtue of their natural frequencies.

Acknowledgment

JH acknowledges Pilkington Glass and SERC for providing chemicals and funding.

Conflict-of-Interest Statement

There are no conflicts of interest in this research article.

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