

Shallow traps for thermally induced hole hopping in DNA

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Received 7 July 2005; accepted 17 January 2006

Available online 14 February 2006

Dedicated to Professor Noel S. Hush on the occasion of his 80th birthday.

Abstract

The theory of thermally induced hopping (TIH) in donor–bridge–acceptor systems for hole transport in DNA duplexes in solution is extended to include energetic theoretical data for the effects of inter-nucleobase interactions. The extended theory incorporates the site specificity of the energetic stabilization of the radical cation of guanine (G), which acts as a resting site for the hole, and of the radical cations of adenine (A), which are accessible by thermal excitation from G^+ ($\Delta = 0.20$ – 0.25 eV). The modified TIH model properly accounts for the flat bridge size dependence of the relative chemical yields for hole transport in $G(A-T)_nGGG$ duplexes ($n = 4$ – 16). This flat, non-ohmic, bridge length dependence is attributed to an energetic gating mechanism, which is induced by energy barriers (~ 0.1 eV) exerted by the proximal and by the terminal edge A groups in the $(A)_n$ bridge, while the interior A groups act as shallow traps for the hole. Our ‘molecular polaron’ model for incoherent, hopping charge transport in solvated DNA is supported by independent theoretical evidence for hole localization induced by intrabase configurational distortions and by polar solvent effects.

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Keywords: Long range charge transport; DNA molecular electronics; Thermally induced hopping

1. Prologue

The exploration of the electronic properties of DNA is of considerable interest in the context of its radiative damage and repair, and for the development of the novel research areas of nanoscience, pertaining to the dynamics, response and function of nanostructures. DNA-based molecular electronic devices are expected to utilize the unique features of recognition, assembly and specific binding properties of the nucleobases, with the DNA duplexes serving as building blocks or/and templates for the assembly and function of electronically active nanoelements. The elucidation of the function of DNA as a ‘molecular wire’ requires the establishment of the mechanisms and dynamics of large transfer and transport in this system [1–8].

The majority of experimental information on charge transport in DNA pertains to hole migration, i.e., the propagation of the radical cation along the duplex [9–20]. Energetic data and computational results [21–25] show that guanine (G) nucleobases act as ‘resting’ lowest-energy sites for holes in DNA duplexes, a concept pioneered by Noel Hush [22]. Theoretical and experimental work showed that GG and GGG doublets/triplets act as shallow hole traps [9–17]. At finite temperatures the concept of hole ‘resting’ sites has to be extended [12,25–30] to involve both the lowest energy G sites and higher energy ($\Delta = 0.20$ – 0.25 eV) [28,30] mediating adenine (A) sites, while high energy ($\Delta = 0.5$ – 0.6 eV) sites involve thymine (T) and cytosine (C).

Two basic issues underlying charge localization, transfer and transport in DNA are structural specificity and energetics control. Regarding structural features we shall distinguish between single component DNA, e.g., poly(G–C), poly(A–T), and structurally disordered DNA. The latter

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involves structurally–positionally disordered DNA, e.g., λ DNA, or structurally disordered DNA containing G sites separated by well characterized (A–T) $_n$ bridges.

1.1. Charge transport in DNA

The following limiting mechanisms of charge transport in molecular wires and in DNA should be considered:

(A) *Band transport.* This mechanism involves coherent charge transport in a narrow band semiconductor in the weak charge scattering limit. The dynamics of the charge scattering process within the narrow band controls the nature of charge transport. On the basis of the Ioffe–Frohlich–Sewall criterion [31] one can infer that coherent transport prevails when the band width B is larger than the scattering width $\hbar/\tau_{\text{scatt}}$, i.e., $B > \hbar/\tau_{\text{scatt}}$, where τ_{scatt} is the relaxation time of the carrier induced by the scattering of medium phonons and intramolecular vibrations, and by medium induced diagonal and off-diagonal disorder. Information on the hole band structure of DNA was inferred from quantum mechanical calculations of the electronic coupling matrix elements for intrastrand hole transfer between neighboring (G⁺G or A⁺A) nucleobases. Undoped, neat, single-component DNA constitutes a large gap (~ 3.5 eV), narrow band ($B \sim 0.1$ eV) semiconductor. If such a model would be applicable to DNA, it could possibly be realized in a single-component duplex. On the other hand, for structurally disordered DNA such a mechanism is definitely inapplicable due to diagonal and off-diagonal disorder effects, which destroy the band structure and result in charge localization.

(B) *Incoherent charge hopping.* In this limit two cases, determined by structural specificity, should be considered.

(B.1) *Single component DNA.* In such a system we expect that incoherent charge hopping will dominate, provided that the band width is smaller than the scattering width [31], i.e., $B < \hbar/\tau_{\text{scatt}}$. In this strong-scattering limit, charge transport in the single component system is accompanied by dephasing at each nucleobase site, which induces charge hopping between nearest neighbors.

(B.2) *Structurally disordered DNA.* Structural disorder induced hole localization on each G site essentially corresponds to dephasing at each hole ‘resting’ site, with G⁺ \rightarrow G hole hopping between guanines which are separated by (T–A) mediating bridges.

For both (B.1) and (B.2) structures, charge hopping in DNA is described in terms of the quantum mechanical non-adiabatic theory [25,28–30,32–36], a field to which important contributions were made by Noel Hush [37–45]. The hopping rates between the G resting sites, between the resting and the bridge sites G and A, and between the A bridge sites, are each described in terms of electronic (direct exchange or superexchange) coupling [32–36], nuclear coupling with a low-frequency medium, and intermolecular modes together with high-frequency intramolecular modes [25,28–30,32–36]. This approach can be considered as an extension of the Holstein small polaron model [46] in the

non-adiabatic limit, which was extended to account for the important effects of intramolecular nuclear distortions (reorganization) of the nucleobasis. This picture of a ‘molecular polaron’ in DNA, which is realized in the strong scattering limit of incoherent charge hopping, is considerably more complete, informative and predictive than simplified polaron models [47], which described each nucleobase in terms of a structureless site and disregarded the effects of the medium reorganization energy.

1.2. Superexchange and thermally induced hole hopping in G⁺(T–A) $_n$ GGG duplexes

It was inferred from a wealth of experimental data [9–20] and their theoretical–computational analyses that charge transport in structurally disordered and structurally–positionally disordered DNA at room temperature in solution proceeds via initial hole injection to G followed by incoherent hopping between adjacent G nucleobases. In this paper we address hole hopping in bridged G⁺(T–A) $_n$ GGG ($n = 1–20$) duplexes, which are of considerable interest in the context of charge transport in the exploration of molecular nanowires. Experimental evidence for long-range hole transport is deduced from measurements of terminal/proximal (GGG)⁺/G⁺ relative chemical yields on long-range (10–200 Å) distance scales in G(T–A) $_n$ GGG duplexes [12,27]. Hole injection into the proximal G occurred from the electronically excited (e.g., Rh⁺³ complexes [11,12] or anthraquinone [19,20]) donor or from a chemical hole shift (from a sugar cation [16–18,27]). Subsequent work by Williams and Barton [48] demonstrated that for photochemical hole injection the relative chemical yields data depend on the nature of the donor, due to side and back reactions. This complication does not prevail for the data of Giese et al. [27], which is based on the hole shift injection in the ground electronic state, which will be used in our analysis of hole hopping. Two mechanisms are applicable for the incoherent charge transport limit in G(A–T) $_n$ GGG duplexes at finite temperatures [27,28,30]. First, the superexchange mechanism [32–35] for G⁺ \rightarrow GGG hole transfer mediated by off-resonance electronic coupling with short (T–A) $_n$ ($n < 4$) bridges. The superexchange interaction for the electronic coupling [32–35] (whose historical background is reviewed in Refs. [36,49]), which induces electron transfer via bridges in systems with an appropriate off-resonance level structure, is ubiquitous in large chemical scale systems [36] in proteins [49] and in DNA [32–35]. The unistep rate exhibits an exponential distance dependence. Second, thermally induced hopping (TIH) via the (A) $_n$ chain occurs in long ($n > 4$) duplexes. The TIH mechanism [28–30,34] prevails in the donor-bridge-acceptor system at a finite temperature, with the donor and the acceptor states being lower in energy than the bridge states. Thermal activation from the donor to the initial site of the bridge is followed by reversible charge hopping within the bridge and subsequently involves charge trapping by the acceptor from the terminal site of

the bridge. All the individual steps in the TIH involve incoherent charge hopping between nearest neighbors. TIH in $G(A-T)_nGGG$ duplexes involves thermally activated charge transfer from G to its nearest-neighbor A in the $(A)_n$ chain, followed by hopping transport in the long ($n > 3-4$) chain to the terminal GGG hole trap. The TIH mechanism manifests a weak distance dependence and allows for very long-range hole transport in DNA.

1.3. Aims and claims

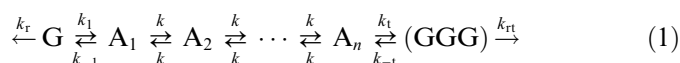
We advanced and applied a kinetic-quantum mechanical model [25,28–40,44–46,49] for hole transport in DNA duplexes, which rests on quantum mechanical non-adiabatic intersite hopping rates in conjunction with kinetic schemes, to describe the compound mechanism of superexchange TIH transport in $G^+(A-T)_nGGG$ duplexes (Fig. 1). This model accounted well for the ‘transition’ from exponential distance dependent superexchange to an algebraic distance dependence of TIH (occurring at $n = 3-4$), in accordance with the experimental data [26,27]. However, the kinetic-quantum mechanical model for the chemical yields failed to describe the experimental bridge size and distance dependence of the ratios of the chemical yields. The experimental results of Giese et al. [27] reveal an independent value (within experimental uncertainty) of the relative chemical yield from $n = 5$ to $n = 16$, while theoretical analyses (Section 2.1 below) predicted a pronounced decrease of this ratio with increasing n . This dichotomy between the weak distance dependence predicted theoretically, and the flat distance ‘independence’ observed in

real-life, raises interesting issues concerning transport in nanostructures. The flat distance dependence of the relative yields was tentatively attributed by us [30] to an energetic gating mechanism, however, the nature of this gating could not be specified. Concurrently, Renger and Marcus [50] proposed that TIH involves two competing channels, i.e., hopping via localized states and transfer through partly delocalized states, thus introducing coherent transport. In this paper, we adhere to the incoherent charge transport picture, extending the TIH model to include energetic information from quantum mechanical calculations. The energetic information implies that the equidistant $(A)_n$ chain involved in TIH is not isoenergetic, with the edge A sites near G and GGG being of different energies and forming barriers for charge injection into the chain. Thus, charge transport within the chain occurs within a spatially extended shallow trap. The extended kinetic-quantum mechanical model accounts well for the extremely weak bridge size dependence for hole transport in DNA in solution.

2. Thermally induced hopping

2.1. The regular TIH model

In the simplest regular model for TIH, all the A bridge units are assumed to be isoenergetic (Fig. 1). For sufficiently long $(A-T)_n$ ($n > 4$) bridges, where the contribution of the superexchange channel is negligible, the kinetic scheme for TIH in the $G(A_1A_2 \dots A_n)GGG$ duplex is



where the hole is initially located on the terminal G. Here, k_1 is the $G^+ \rightarrow A_1$ thermal excitation rate of the hole from the donor (G) to the bridge A_1 molecule, k_{-1} is the $A_1^+ \rightarrow G$ hole detrapping rate, and k are the hopping rates between nearest-neighbor A nucleobases within the bridge. The $A_n^+ \rightarrow GGG$ trapping rate is k_t , while k_{-t} is the $GGG \rightarrow A_n$ hole detrapping. The irreversible chemical reactions with water have the rate constants k_r at G^+ and k_{rt} at $(GGG)^+$. The chemical yields of the reaction products at G and $(GGG)^+$ are denoted by Y_G and Y_{GGG} , respectively, and the relative yield is given by $R = Y_{GGG}/Y_G$. This kinetic scheme results in an analytical expression for the relative chemical yield [30]

$$R = \left(\frac{k_{rt}}{k_r} \right) \frac{k_1 k_t}{k_{-1} k_{-1} + k_t k_{rt} + k_{rt} k_{-1} \left[1 + \frac{k_t}{k} (n-1) \right]} \quad (2)$$

The individual rates appearing in Eq. (2) were inferred [30] from quantum mechanical calculations of the pair electronic matrix elements [24,49]. The nuclear Franck–Condon factors were estimated from theoretical calculations of the energetics, and rough estimates of intermolecular and intramolecular couplings [30], Eq. (2). The relative chemical yield was expressed in the algebraic form $Y = \tilde{C}/(\tilde{A} + \tilde{B}n)$, where \tilde{A} , \tilde{B} and \tilde{C} are numerical constants.

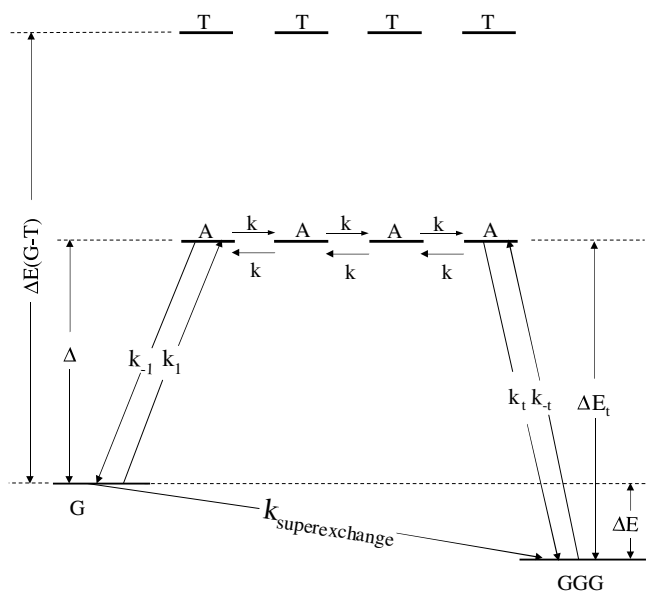


Fig. 1. An approximate energetic scheme for hole transport in $G(A-T)_nGGG$ duplexes, Eq. (3), with all the A bridge nucleobases being isoenergetic. For short bridges ($n < 3-4$) the superexchange mechanism dominates. For longer bridges ($n \geq 4$) the regular TIH model is expected to set in (see text).

On the basis of our previous analysis of the individual rates [30] it is impossible to reconcile the experimental ‘flat’ distance dependence of R with the predictions of Eq. (2). A model that will be able to explain the experimental data should include an element of retardation of the back transfer from the bridge. Indeed, when $k_{-1} = 0$, R (Eq. (2)) is independent of n . We require an energetic gating mechanism, where the probability for the hole to return from the bridge to the donor is effectively blocked.

In the DNA duplex the energetics, electronic couplings and other properties depend on the local inter-nucleobase and solvent environment. The regular model, with equal hopping rate constants along the bridge, constitutes a simplified abstraction and should be extended to describe realistic cases. In particular, one should distinguish between the A nucleobases inside the bridge and the A nucleobases at both ends of the bridge. Quantum chemical calculations [24] showed that the internal A^+ cation radicals have a lower energy than the two terminal A_1^+ and A_n^+ cation radicals. These energy barriers for the A^+ radical ion configuration at the end of the bridge will manifest a marked effect on charge transport.

2.2. Energetics

The energetics of cation radicals in different nucleotide triplets $5'$ -XBY- $3'$ in DNA (X,B,Y = A,G,C,T) was estimated from the quantum mechanical NDDO-G scheme [24]. A significant finding was that the stabilization of B^+ in $5'$ -X(B^+)Y- $3'$ is site-specific, and is considerably affected by the nature of the neighboring nucleobases, reflecting on intermolecular stabilization effects of the charged nucleobase. This stabilization phenomenon implies that the hole states in Giese’s duplex



(A) $_n$ bridge are not isoenergetic. Rather, the energies of the radical cation states at the edges of the bridge, i.e., $CA_1^+A_2$

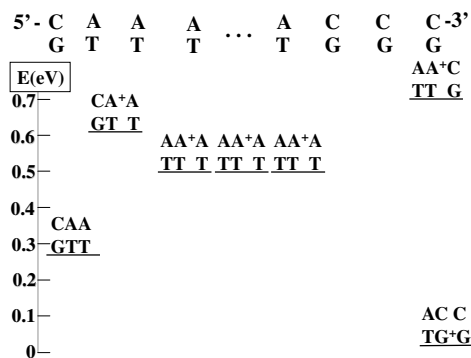


Fig. 2. The energies of the radical cation states in the $G(A-T)_nGGG$ duplex, Eq. (3), as obtained from the quantum mechanical NDDO-G calculations (Ref. [24]). Note the site specificity of the energies of the A^+ sites within the A_n chain.

and $A_{n-1}A_n^+C$, are higher than those of the interior bridge states, i.e., $A_{j-1}A_j^+A_{j+1}$ ($2 \leq j \leq n-2$). In Fig. 2, we summarize the energetic data for the energetics of radical cation states in duplex (3). These involve the following energy gaps:

- (i) Hole injection to A_1 : $\Delta E_1 = E(CA_1^+A_2) - E(TG^+T) = 0.34$ eV.
- (ii) Hole transfer from A_1 to A_2 : $\Delta E_2 = E(A_1A_2^+A_3) - E(CA_1^+A_2) = -0.13$ eV.
- (iii) Hole transfer from A_{n-1} to A_n : $\Delta E_n = E(A_{n-1}A_n^+C) - E(A_{n-2}A_{n-1}^+A_n) = 0.23$ eV.
- (iv) Hole hopping inside the chain: $\Delta E_c = E(A_jA_{j+1}^+A_{j+2}) - E(A_{j-1}A_j^+A_{j+1}) = 0$.
- (v) Hole trapping: $\Delta E_t = E(TG^+G) - E(A_{n-1}A_n^+C) = -0.71$ eV.
- (vi) Hole migration within the trap: $\Delta E_{mt} = E(GG^+G) - E(TG^+G) = -0.03$ eV.

These energetic data for hole states in DNA duplexes disregarded medium solvation effects. Nevertheless, we inferred [29] from a detailed comparison of the available energetic experimental data with these calculations that the theoretical results provide the energetic hierarchy of the hole states, with the energy gap being slightly overestimated (i.e., by a numerical factor of ≤ 2). The energetic data for the $(T-A)_n$ bridge in duplex (2) are presented in Fig. 2. The energetics reveal that barriers of 0.13 eV exist at the onset of the bridge, and of 0.23 eV at the end of the bridge (Fig. 2), whereas the A nucleobases in the interior of the bridge serve as temporal shallow hole traps.

2.3. The modified TIH model

The regular TIH model (Fig. 1) has to be extended to account for the upward shifts of the energies of the

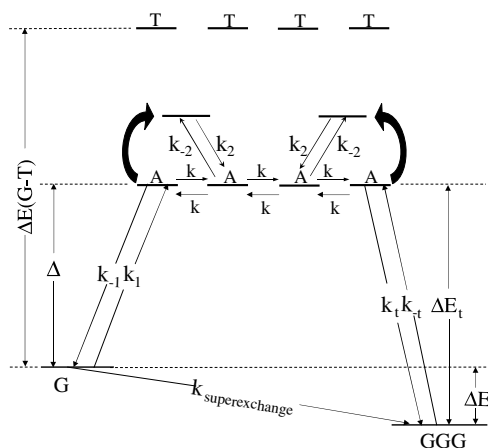
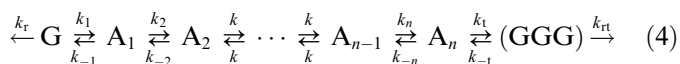


Fig. 3. The TIH scheme for hole transport in $G(A-T)_n$ duplexes, which includes the site specificity of the energies of A sites within the (A) $_n$ bridge. The energies of the proximal and the terminal A^+ radical cations are shifted upward, while the energies of the interior A^+ radical cations within the bridge remain isoenergetic.

proximal A_1 and the terminal A_n nucleotides in the $(A)_n$ bridge (Fig. 2). Based on these observations we generalize the kinetic scheme for the hole transfer (Fig. 3). The first step remains thermal hopping to the closest base of the bridge, with a forward rate constant k_1 and a backward rate constant k_{-1} . From the first base the hole goes down in energy by $E(CA_1^+A_2) - E(A_1A_2^+A_3) = -\Delta E_2$, with the rate constant k_2 . The reverse rate constant is k_{-2} , where $k_{-2}/k_2 = \exp\{[E(A_1A_2^+A_3) - E(CA_1^+A_2)]/k_B T\}$. Subsequently the hole propagates inside the bridge with an equal forward and backward hopping rate constant k . At the end of the bridge the hole has to climb in energy by $E(A_{n-1}A_n^+C) - E(A_{n-2}A_{n-1}A) = \Delta E_n$ to the terminal adenine with a rate constant k_{-n} and back into the bridge with a rate constant k_n . In the last propagation step the hole is transferred from the bridge to the triple GGG with forward and backward rate constants k_t and k_{-t} , respectively. The irreversible water reactions that eliminate the hole have a rate constant k_r at G^+ and k_{rt} at $(GGG)^+$. The model is represented by the following kinetic scheme



2.4. Model calculations

For the regular model we use the results of the quantum mechanical analysis of our previous work (Table 2 of Ref. [30]), which resulted in the following elementary rates for the regular bridge (Fig. 1 and kinetic scheme (1)): $k^{re} = 5 \times 10^7 \text{ s}^{-1}$, $k_1^{re} = 4 \times 10^4 \text{ s}^{-1}$, $k_t^{re} = 4 \times 10^7 \text{ s}^{-1}$ and $k_{-t}^{re} = 1.6 \times 10^2 \text{ s}^{-1}$. Here, the superscript ‘re’ refers to the regular model, labelling each rate constant in the kinetic scheme of Eq. (1) and Fig. 1. In addition, the superexchange rate in the 5'-G⁺TG-3' duplex was estimated [30] as $k_{\text{super}}(1) = 1.2 \times 10^8 \text{ s}^{-1}$. The kinetic information on the irreversible reaction of water with G^+ and $(GGG)^+$ was recently inferred by us from the analysis of the superexchange rate $k_{\text{super}}(n)$, which included the effect of the distance dependence of the reorganization energy on this rate [51]. This analysis resulted in $k_r/k_{\text{super}}(1) \simeq 8 \times 10^{-5}$ and $k_{rt}/k_{\text{super}}(1) = 4 \times 10^{-4}$ [51]. As $k_{\text{super}}(1)/k^{re} \simeq 1$ [30], we infer that $k_r/k^{re} \simeq 8 \times 10^{-5}$ and $k_{rt}/k^{re} \simeq 4 \times 10^{-4}$. Model calculations of R , Eq. (2), for the regular bridge model, Eq. (1), were performed using the kinetic parameters given above, with each rate being normalized by k^{re} . These results (Fig. 4) exhibit a marked bridge length dependence, in variance with experimental data [24].

The kinetic parameters for the modified TIH model (Fig. 3) and for the kinetic scheme, Eq. (4), can be obtained in a similar way to the estimates of the kinetic data for the regular bridge [30], with the modified energetic data of Section 2.2. All the kinetic data for the modified TIH will be normalized by the hopping rate k in the $\{A_2 \dots A_{n-1}\}$ interior part of the bridge. This hopping rate is identical for the modified bridge and for the regular bridge, i.e.,

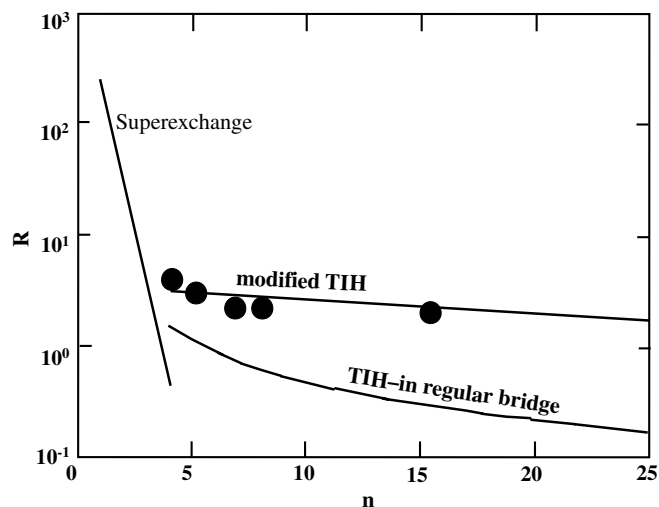


Fig. 4. The analysis of the experimental data (●) of Giese et al. [27] for the relative chemical yields in the $G(A-T)_nGGG$ duplex, Eq. (3), according to the TIH model. The lower line marked “TIH in regular bridge” represents the results of the regular TIH model, Eq. (2), with all the A^+ sites within the $(A)_n$ chain being isoenergetic, with the kinetic rate constants adopted from Ref. [30]. The curve marked “modified TIH” represents the results of the extended TIH model to account for the site specificity of the energies of the A^+ sites, according to Fig. 3 and to kinetic scheme (4), with the kinetic-quantum mechanical parameters from Eq. (5) being given in the text. Note that the effect of shallow hole trapping within the interior A^+ sites in the $(A)_n$ bridge induces a flat bridge length dependence of the hole transport yield. For the sake of completeness we also present on the LHS of the figure an exponential curve marked “superexchange”, which represents the $G^+ \rightarrow GGG$ superexchange driven relative yield [27,51], which dominates for short $(T-A)_n$ ($n < 3-4$) bridges.

$k = k^{re}$. A general expression for the normalized rates between close neighbor bases can be expressed by the traditional electron transfer theory:

$$\frac{k_j}{k} = \left(\frac{V_j}{V}\right)^2 \exp\left[-\left(\Delta E_j^2 + 2\lambda\Delta E_j\right)/4\lambda k_B T\right] \quad (5)$$

where $j = 1, -1, 2, -2, n, -n, t, -t$, with the indices labelling the rates in scheme (4). The energy gaps ΔE_j correspond to the rates k_j . It is assumed that the reorganization energies λ and the intramolecular Franck–Condon factors are similar for all hole transfer processes between nearest-neighbor nucleobases. On the basis of the analysis of Section 2.2, we estimate the energy gaps to be lower by 30–40% than the theoretical estimates [24], which disregard medium solvation effects, taking $\Delta E_1 = 0.2 \text{ eV}$ and $\Delta E_2 = \Delta E_n = 0.1 \text{ eV}$. We used the electronic couplings and the reorganization energy from our previous work [30]. With these parameters, the relative rates are: $k_1/k = 10^{-4}$, $k_{-1}/k = 10$, $k_2/k = 7$, $k_{-2}/k = 0.13$, $k_t/k = 1.5$ and $k_{-t}/k = 10^{-6}$. The irreversible reaction rates with water were estimated from the analysis of the superexchange rates [51], $k_r/k = 8 \times 10^{-5}$ and $k_{rt}/k = 4 \times 10^{-4}$. These relative rates were used for the solution of the kinetic equation for the scheme given by Eq. (4). The results of the modified kinetic model are presented in Fig. 4, exhibiting a flat, non-ohmic, bridge length dependence, in accordance with the experimental data [27].

3. Concluding remarks

The modified TIH model, which incorporates bridge energetic effects, provides a new physical picture for transient hole trapping within the $A_1A_2 \dots A_n$ bridge, where the hole donor (G)⁺ and acceptor (GGG)⁺ sites are separated from the interior of the bridge ($A_2 \dots A_{n-1}$) by energy barriers on the proximal (A_1) and distal (A_n) bridge elements. Accordingly, the A nucleobases within the interior segment $A_2 \dots A_{n-1}$ of the bridge act as shallow traps in the charge transport process. This physical picture of shallow trapping within the interior of the bridge accounts well for the flat bridge length dependence of the relative chemical yields for hole transport through long A bridges.

Our theoretical treatment rests on incoherent hole hopping between localized radical cation A^+ states in the $(A)_n^+$ bridge, where coherence effects in the hole transport are eroded. A heuristic, qualitative interpretation of the flat bridge length dependence of R can be provided in terms of the alternative mechanism of band transport, i.e., coherent transport. The calculations of Renger and Marcus [50] showed that charge transport via delocalized states does indeed lead to the flattening of the relative chemical yield vs. n dependence. As the chemical yield data provide only limited information on the hole dynamics, at present one has to rely on arguments of ‘good’ agreement between the modified TIH incoherent transport model and experimental data. Such arguments are, of course, only indicative but not conclusive, requiring further experimental and theoretical input. On the experimental front, time-resolved data for the charge transport rates, charge diffusion coefficient, or mobility within the A_n chain in solution, will resolve this issue. In spite of extensive experimental efforts in this field, these time-resolved data are not yet available. On the theoretical front, quantum mechanical calculations provide strong evidence for hole localization on a single nucleobase in DNA duplexes. Olofsson and Larsson [52] studied the effects of structural reorganization of the nucleobases on the delocalization of charge in DNA, establishing energetic stabilization of a localized hole due to intrabase configurational distortions. Voityuk [53] reported that solvation effects result in the suppression of hole delocalization in $(GC)_n$ duplexes, resulting in complete localization of the hole on individual guanines. This independent theoretical evidence for hole localization, which is induced by interbase and polar solvent interactions, provides strong support for our ‘molecular polaron’ model for incoherent, hopping charge transport in solvated DNA.

Acknowledgement

This research was supported by the European Grant for Future and Emerging Technologies (IST-2001-38951).

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