FEATURE ARTICLE

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Recent developments of charge injection and charge transfer in DNA

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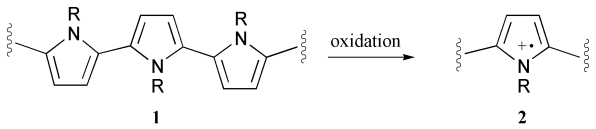
The question of whether and how electrons migrate through DNA was a matter of controversial discussion over the last ten years. Today, there is no doubt that long distance charge migration through DNA exists and most scientists explain this process by a multistep hopping mechanism. This feature article presents recent developments of our group on the injection of a positive charge into DNA bases and the transfer of the charge between the DNA bases. The influence of the donor, the nature of the bridge, and the distance between the donor and the acceptor are discussed.

I Introduction

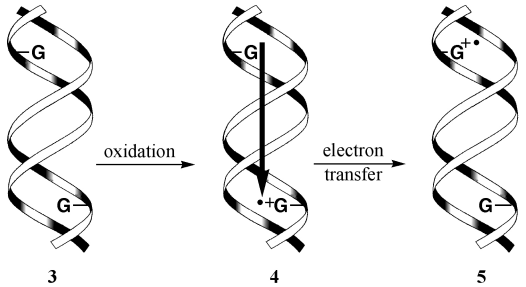
The Nobel Prize in Chemistry 2000 was awarded to Alan J. Heeger,[1] Alan G. McDiarmid,[2] and Hideki Shirakawa[3] 'for the discovery and development of conductive polymers'. In its press release the Royal Swedish Academy of Science says that 'this year's Nobel laureates in Chemistry are being rewarded for their revolutionary discovery that plastics can, *after certain modifications*, be made electrically conductive'. These modifications are, for instance oxidation reactions that transform heterocyclic functional groups of polymers like **1** into radical cations **2** (Scheme 1). Because the positive charge migrates between the heterocycles, the insulating polymeric material can become electrically conductive.



1 **2**

Scheme 1

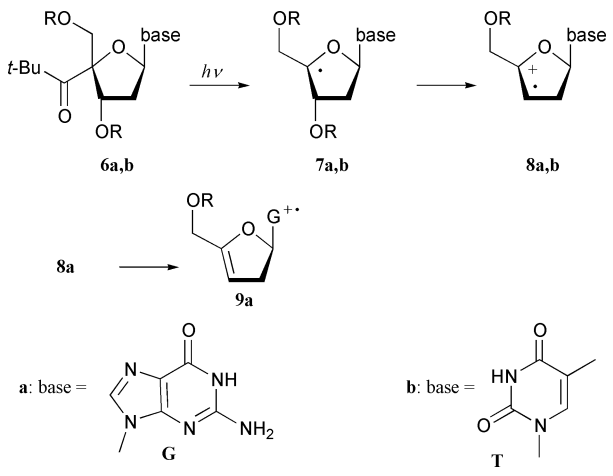
A few years ago, J. Jortner *et al.*[4] and our group[5] have asked the related question whether a migration of the positive charge can also occur between the heterocycles of DNA, especially the guanines that have the lowest ionization potential of all four DNA bases (Scheme 2).[6] The difference between polymer **1** and DNA **3** is that the heterocycles in **1** are directly connected with each other whereas those in DNA **3** are separated from each other by sugar phosphate spacers.[7] In order to answer the question on charge transfer through DNA, we developed a method for site selective oxidation of a single guanine (**3** → **4**) and for the detection of the charge transfer between the guanines (**4** → **5**).[5]



3 **4** **5**

Scheme 2

Our assay uses 4′-pivaloylated nucleotides, **6a**, **b** which are incorporated into DNA strands. Photolysis of **6a**, **b** leads *via* radicals **7a**, **b** to the enol ether radical cations **8a**, **b** (Scheme 3).[8]



Scheme 3

These carbohydrate radical cations are strong oxidants that quantitatively oxidize a guanine base that is situated at its anomeric carbon atom (**8a** → **9a**).[9]

In contrast to guanine (G), the base of lowest ionization potential of the four nucleobases, thymine (T) at the anomeric center of carbohydrate radical cation **8b** is not oxidized, but the positive charge can be injected into an adjacent G (**10** → **11**) of the DNA double strand (Scheme 4).[8] In this feature article we will describe how (a) this charge injection from the enol ether radical cation into an adjacent guanine (**10** → **11**) or guanine derivative, and (b) the charge transfer between the guanines (**4** → **5**) is influenced by the sequence of the bridge and the distance between the electron donor and electron acceptor. Because of the fast progress in this research area, we will focus the attention mainly on our results of the last two years.

Bernd Giese studied chemistry in Heidelberg, Hamburg, and Munich, where he received his Ph.D. in 1969. After two years in the pharmaceutical industry (BASF) he became Privat-Dozent in Freiberg/Germany in 1976. From 1977 to 1988 he was full Professor in Darmstadt and joined the University of Basel/ Switzerland in 1989. His research interests are focused on radicals in chemical and biological systems.

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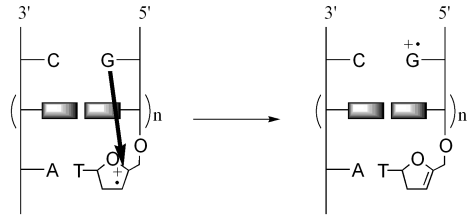


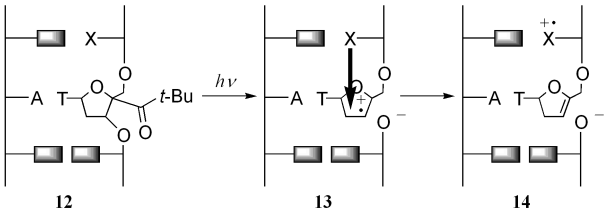
10 **11**

Scheme 4

II Charge injection

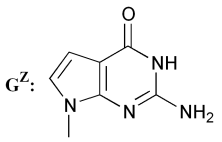
1 Method

The positive charge was injected into the DNA bases using strands like **12** carrying site-selectively a 4′-pivaloylated thymidine. It has turned out that enol ether radical cation **13**, generated by photolysis of the 4′-pivaloylated thymidine **12**, cannot oxidize pyrimidines or an adenine of the adjacent base pairs (Scheme 5).[8,10] As the yield of the enol ether **14** shows,



12 **13** **14**

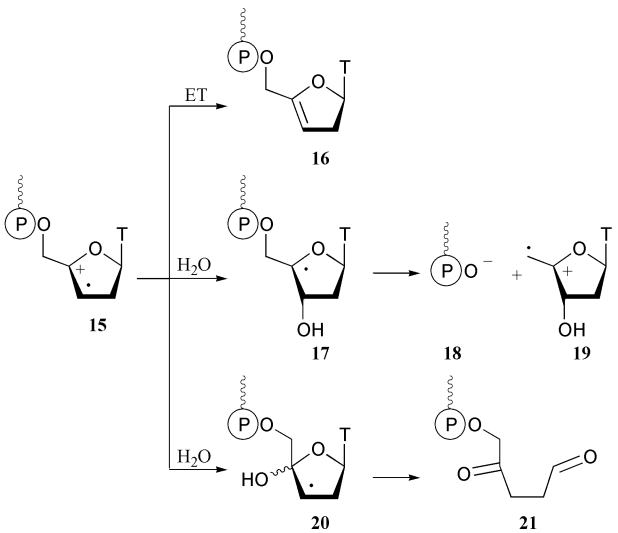
X	**14** yield (%)
G	46
A	<2
T	<2
G^Z	95



Scheme 5

electron transfer occurs only if a guanine, the nucleobase of lowest ionization potential, is situated close to the oxidant. We have also observed that the efficiency of this charge injection increases from 46% to 95% if instead of guanine (G) a 7-deazaguanine (G^Z) is used,[10] which has an even lower ionization potential than G (Scheme 5).[11]

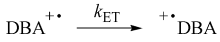
In competition to the charge transfer step (**15** → **16**) the radical cation **15** is trapped by water, which leads after several subsequent steps to **18** and **21** as stable reaction products (Scheme 6).[8,12] Using HPLC as the analytical method, we could show that products **16**, **18** and **21** are formed in more than 95% yield from enol ether radical cation **15** under anaerobic conditions in water. Thus, from the product ratio **16**/(**18** + **21**) the relative rate of the electron transfer step **15** → **16** can be deduced. In independent experiments we could also measure the absolute pseudo-first order rates of the water trapping reactions (**15** → **17** + **20**). With these data the absolute rate coefficients of the electron transfer steps could be deduced.[8]



15 **16** **17** **18** **19** **20** **21**

Scheme 6

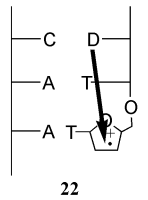
Using this method the influence of the electron donor D, the nature of the bridge B, and the distance between the donor D and the acceptor A on the electron transfer rate k_{ET} were determined (Scheme 7).



Scheme 7

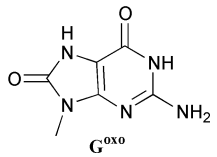
2 Influence of the electron donor

Experiments with DNA strands **13** and **22** have shown that an electron transfer can compete with the water trapping reaction only if the ionization potentials of the heterocyclic bases are as low as that of guanine. With unnatural bases like 8-oxoguanine (G^{oxo}) or 7-deazaguanine (G^Z), which have lower ionization potentials than G, the efficiency of the electron transfer increases (Fig. 1).[8,10]



22

D	k_{ET} (10^6 s^{-1})
G	1.2
G^{oxo}	4.6
G^Z	20



G^{oxo}

Fig. 1 Influence of the electron donor D on the electron transfer rate k_{ET} through DNA sequence **22**. The experiments were carried out with long double stranded oligomers, and the carbohydrate radical cation was generated from a 4′-pivaloylated thymidine as shown in Scheme 5. The rates were determined by competition kinetic experiments.

Because the experimental errors were smallest with G^Z as electron donor, we preferentially used this base for studying the influence of the nature and the length of the bridge on the charge injection rate.

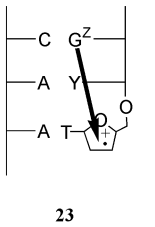
3 Nature of the bridge

In DNA double strand **23** thymine (T) of an A:T base pair, situated between the electron donor G^Z and the enol ether radical cation (electron acceptor), is exchanged by difluorotoluene, benzene, or adenine. As the experimental results in Fig. 2 demonstrate, this has only a very small effect on the electron transfer rate. Thus, the nature of the π-system plays only a minor role as long as its ionization potential is much higher than that of G.

But the charge injection step in double strand **23e**, which contains one abasic site (hydrogen instead of a π-system at C–1 of the deoxyribose) between donor and acceptor, is much faster. We explain this by an increase of local flexibility near the abasic site,[13] which brings the electron donor and the electron acceptor closer to each other. This explanation is in accord with charge injection experiments in conformationally flexible single strands that are, in general, faster than in double strands.[8,14]

4 Length of the bridge

In order to determine the influence of the bridge length on the electron transfer rate, we generated DNA systems **24**, where the



23

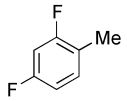
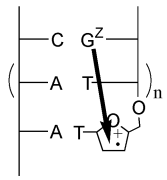
	Y	k_{ET} (10^6 s^{-1})
a:	T	20
b:		11
c:		23
d:	A	16
e:	H	140

Fig. 2 Influence of the bridge Y on the electron transfer rate k_{ET} through DNA sequence **23**. The experiments were carried out with long double stranded oligomers, and the carbohydrate radical cation was generated from a 4′-pivaloylated thymidine as shown in Scheme 5. The rates were determined by competition kinetic experiments.

distance between the electron donor (G^Z) and the electron acceptor (enol ether radical cation) was increased by increasing the number of A:T base pairs between them. The data in Fig. 3 show that an increase of the bridge length (about 3.4 Å per A:T base pair) drastically slows down the electron transfer rate.



24

n	Δr (Å)	k_{ET} (10^6 s^{-1})
0	6.1	1100
1	9.5	20
2	12.9	5.0
3	16.1	1.3

Fig. 3 Influence of the distance Δ*r* between the base G^Z (electron donor) and the carbohydrate radical cation (electron acceptor) on the electron transfer rate k_{ET} in the DNA sequence **24**. The experiments were carried out with long double stranded oligomers, and the carbohydrate radical cation was generated from a 4'-pivaloylated thymidine as shown in Scheme 5. The rates were determined by competition kinetic experiments.

The distance influence on the electron transfer rate is often expressed by the Marcus–Levich–Jortner eqn. (1),[15] which predicts a logarithmic correlation between the electron transfer rate k_{ET} and the distance Δ*r*. The proportionality factor β describes the ability of the molecule to transport electrons.

$$\log k_{ET} \propto -\beta \cdot \Delta r \qquad (1)$$

A plot of the charge injection rates in double strand **24** (Fig. 4) demonstrates that eqn. (1) holds only if the distance between the electron donor and electron acceptor is longer than 9 Å. At shorter distances the electron transfer occurs faster than predicted by eqn. (1).

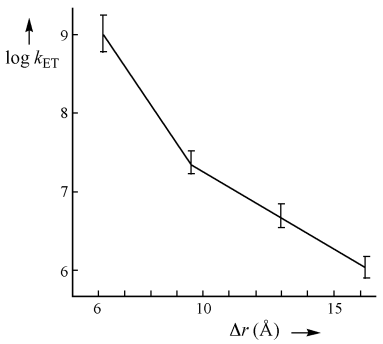


Fig. 4 Logarithmic plot of the electron transfer rates (k_{ET}) against the distance (Δ*r*) between donor and acceptor in the DNA sequence **24**.

Such a rate increase at short distances has also been observed recently by M. E. Michel-Beyerle and coworkers,[16] who measured absolute charge shift rates between a photoactivated acridinium ion and G^Z. They explained this effect by an influence of the solvent reorganization energy. The Marcus equation correlates the electron transfer rate *k* with the Gibbs free energy Δ*G*, the electronic coupling *V*, and the reorganization energy λ (eqn. (2)).[17]

$$k_{ET} = f(\Delta G, V, \lambda) \qquad (2)$$

But the distance dependence of the charge transfer described by correlation (1) takes only the electronic coupling into account. If a charge is transferred in a highly polar solvent like water, where the solvation effects are large, also the solvent reorganization energies could be a function of the distance.[16] The solvent reorganization is small for charge shifts over very short distances, it increases with its length until it reaches a plateau.[16] Above this distance, the solvent reorganization energy remains constant and eqn. (1) can be applied. This explanation is in accord with the experimental results of Figs. 3 and 4. The rates between 9.5 and 16.1 Å exhibit a logarithmic correlation with the distance ($\beta = 0.55 \pm 0.1$ Å^{-1}). But at shorter distances the charge injection is faster than expected from eqn. (1). This effect explains the high β-values of charge shift experiments over relatively short distances, which were described earlier by us[8] and by Fukui and Tanaka.[18]

III Charge transfer between guanines

1 Method

The charge injection step described in Section II generates a guanine radical cation ($G^{\cdot+}$), which starts the electron transfer between the guanines. The influence of the distance and the sequence on this charge transfer will be discussed in this Section. The positive charge at the guanines in DNA can be detected by trapping of $G^{\cdot+}$ with water. This leads, after treatment with enzymes or bases,[5] to cleavage products P_G that are analyzed by gel electrophoresis. A typical example is shown in Fig. 5.[19]

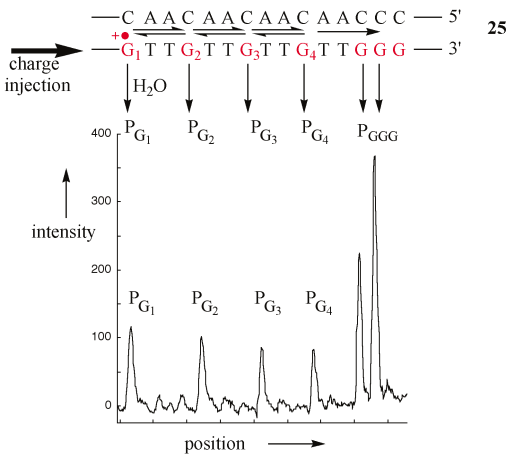


Fig. 5 Histograms of denaturating polyacrylamide gels, obtained by substraction of control experiments from irradiation experiments with modified strands, which contain a 4'-pivaloyl thymidine as in **12**. The histogram shows the yields of products P_G and P_{GGG} at various positions. These products are formed by water trapping of the guanine radical cations and subsequent selective strand cleavage.

The formation of the water-trapping products P_G and P_{GGG} shows that the guanines are charge carriers. The positive charge starts from G_1 in **25**, migrates in reversible transfer steps between the single guanines, until it reaches the GGG unit, which is a sink for the positive charge. The amounts and the

ratios of the trapping products P_G and P_{GGG} depend upon the rates of the electron transfer (k_{ET}) and of the water trapping (k_{H_2O}) reactions.[20] Both reactions are influenced by the reaction conditions, for example the pH value. Therefore one should compare yield data of only those experiments that are carried out under similar conditions. The absolute rate of the charge transfer between guanines was measured by F. D. Lewis and coworkers.[21] Using their rate data and our yield data, the migration of the positive charge between the guanines from G_1 to GGG and the formation of the products P_G and P_{GGG} could be calculated. Fig. 6 demonstrates that the water trapping reaction

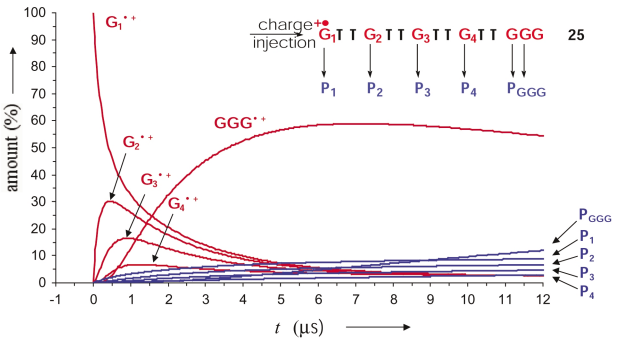


Fig. 6 Migration of the positive charge from G_1 to GGG through DNA **25** (only one strand is shown) and formation of products P_1 to P_{GGG} by water trapping of the guanine radical cations as a function of time. The results are calculated by solving kinetic equations using the rate data of F. D. Lewis[21] and our[20] yield data.

of the positive charge at the guanines G_1 to G_4 is slower than the charge transfer over two A:T base pairs (10.5 Å). As a consequence, the product ratios do not yield directly the electron transfer rates.[20,22]

In an extreme case where all electron transfer steps are reversible and much faster than the water trapping reactions, the product ratios mainly reflect the thermodynamic charge stabilizations of the charge carriers and the rates of their water trapping reactions. Thus, experiments with DNA strands having identical charge carriers at the beginning and at the end (for example GG doublets) could fake a distance independent charge transfer. Another consequence of this situation is that intermediate charge carriers, like single Gs, where the positive charge is nearly 10 times less stabilized than on GG,[21] could give product yields that are too small to be detected by gel electrophoresis. In our experiments, a GGG sequence was always used as a nearly irreversible trap of the positive charge and as a driving force for the reaction.

2 Charge transfer between guanines

Recently, we have shown that the transfer of a positive charge between a $G^{\cdot+}$ and the GGG trap in **26**, which are separated from each other by $(A:T)_n$ bridges, follows two different mechanisms.[23] At short distances the rate depends strongly on the length of the $(A:T)_n$ bridge (Fig. 7). This is in accord with a direct, single step charge transfer, which can be described by the Marcus–Levitch–Jortner eqn. (1). The β-value of this process is 0.6 Å^{-1}.

But with very long $(A:T)_n$ sequences the distance dependence nearly vanishes (Fig. 7). This clearly demonstrates a change in the reaction mechanism. Obviously, with very long $(A:T)_n$ sequences the distance dependent, single step charge transfer between the guanines is so slow that a new, nearly distance independent reaction can compete. We have described

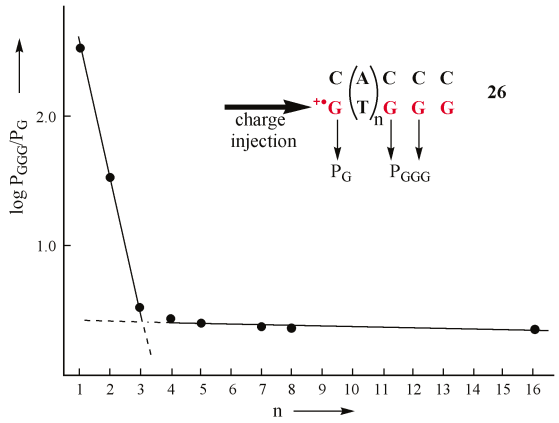


Fig. 7 Plot of $\log(P_{GGG}/P_G)$ against the number n of A:T base pairs between $G^{\cdot+}$ and GGG in the DNA sequence **26**. The steep line corresponds to the strong distance dependence of the single step charge transfer described by eqn. (1). The flat line shows the weak distance dependence of the activated hopping process involving also adenines as charge carriers, described by eqn. (3).

this new process as a multistep reaction, in which also the adenines act as charge carriers (Fig. 8).[20,23] The rate determining step is the endothermic oxidation of an adenine, which is adjacent to $G^{\cdot+}$. The positive charge then migrates over the $(A:T)_n$ sequence until it reaches the next guanine. Because the thermoneutral charge transfer steps between adjacent adenines (k_{AA}) are much faster than the endothermic oxidation of A by $G^{\cdot+}$ (k_{GA}) the length of the $(A:T)_n$ sequence plays only a minor role.

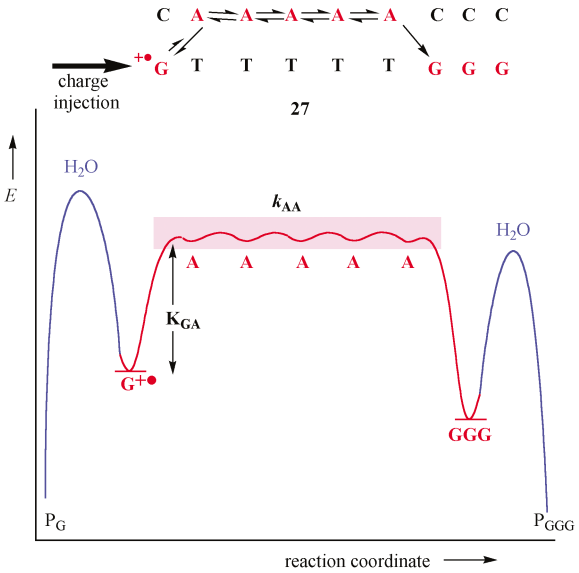


Fig. 8 Reaction profile for the thermally activated hopping process in DNA sequence **27** where guanines as well as adenines are the charge carriers. The water trapping reactions of the guanine radical cations are shown in blue. Not shown are the water trapping reactions of the positive charge at the adenines. Their transition states should be much higher than those of the $G^{\cdot+}$ trapping reactions. Decisive for the rate of the overall charge transport is the equilibrium constant K_{GA} (equilibration of the charge in GA sequences of double strands) and the rate of the charge transfer between adjacent adenines k_{AA}.

A simple description of this process is given by eqn. (3) where k_{ET} is the overall rate coefficient of the electron transfer between GGG and $G^{\cdot+}$, and N is the number of the charge transfer steps between the adenines.[24]

$$1/k_{ET} = 1/k_{GA} + N/k_{AA} \quad (3)$$

It is obvious that a change of the mechanism from a single step to a thermally activated hopping process, where also adenines act as charge carriers, depends upon the difference of the oxidation potentials of the bases A and G (K_{GA}). If N reaches the value k_{AA}/k_{GA}, then the length of the bridge will influence the overall rate of the charge transfer again.

3 Charge hopping

The experiments of J. K. Barton,[25] G. B. Schuster,[26] and our group[5] in the last few years have clearly demonstrated that transfer of a positive charge between the guanines in mixed DNA double strands occurs over very long distances (Fig. 9).

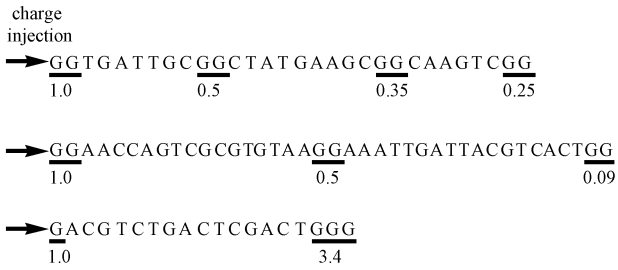


Fig. 9 Efficiency of the transport of a positive charge through DNA double strands (only single strands are shown). The numbers give the relative yields of the water trapping reactions of the various guanines, they are normalized to 1.0 at the beginning of the charge transport.

Today, there is a consensus that these processes happen *via* a multistep hopping mechanism in which the charge migrates in a reversible diffusion between charge carriers. The nature of the charge carriers is still under discussion, we favour an explanation where all guanines and, if the $(A:T)_n$ sequences are long, also adenines are the charge carriers.

This mechanism is in accord with charge transport experiments of DNA strands where mismatches had been induced either into G:C or A:T base pairs.[19] In strands **29** and **30** cytosine (C) of the charge carrying G:C base pair is exchanged by thymine (T) or by an abasic site (H).

As the data in Fig. 10 show, these mismatches cause a dramatic decrease of the efficiency of the charge transport to the

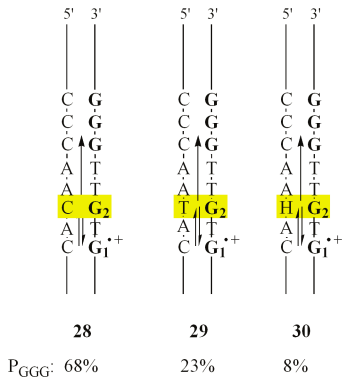
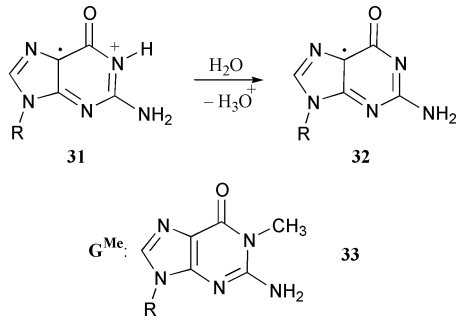


Fig. 10 Efficiency of the transfer of the positive charge from $G_1^{\bullet+}$ to GGG in **28**–**30**. The efficiency is measured as the yield of the water trapping product P_{GGG} at the GGG sequence. The total sum of the water trapping products is set to 100%. Mismatches of the G:C base pair reduce this efficiency. The symbol H stands for an abasic site, where the base is exchanged by hydrogen.

GGG sequence from 68% (**28**) to 23% (**29**), and 8% (**30**). We have explained this effect by a proton transfer in the mismatched pairs from the charge carrier $G^{\bullet+}$ to water.[19] The resulting guanosyl radical **32** is a much poorer oxidant and slows down or stops the charge transport (Scheme 8).



Scheme 8

This mechanism could be proven in experiments with the methylated guanine **33** (G^{Me}), where the acidic proton at N–3 is absent. Incorporation of G^{Me} into strand **34** shows that the charge transport becomes efficient again although an abasic site is opposite to G^{Me} (Fig. 11).[27]

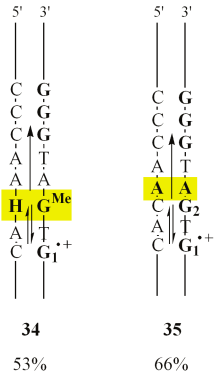


Fig. 11 Efficiency of the transfer of the positive charge from $G_1^{\bullet+}$ to GGG in **34** and **35**. The efficiency is measured as the yield of the water trapping product P_{GGG} at the GGG sequence. The total sum of the water trapping products is set to 100%.

In contrast to mismatches in the charge carriers G:C, a mismatch of A:T base pairs plays only a minor role, if the $(A:T)_n$ sequences are short. Thus, the exchange of the A:T base pair of **28** by an A:A mismatch (**35**) for example reduces the charge transport efficiency only slightly.[19] This is reasonable because adenines in short $(A:T)_n$ sequences are not charge carriers so that the proton transfer to the water should be slow.[28]

IV Conclusion

A positive charge injected into a guanine, the nucleobase of lowest ionization potential, does not remain located at this heterocycle but it migrates in a multistep hopping reaction through DNA over long distances. Intermediates of this diffusion process are charge carriers (mainly guanines), at which the positive charge has a certain lifetime. These relay stations are separated from each other by $(A:T)_n$ bridges that mediate the charge transfer but do not act as charge carriers. Increasing the length of these bridges slows down the single step charge transfer between the guanines. As a consequence, at long $(A:T)_n$ sequences the endothermic oxidation of an adenine adjacent to $G^{\bullet+}$ can become faster than the direct charge transfer to the distant guanine. Now, also adenines become charge carriers of the hopping process. Side reactions like proton transfer to or nucleophilic attack by the surrounding water (or other bases and nucleophiles) reduce the efficiencies of these

hopping processes, which therefore depend upon the structure and flexibility of the DNA as well as on the medium.

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