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## Hole Transport Between G Bases in DNA

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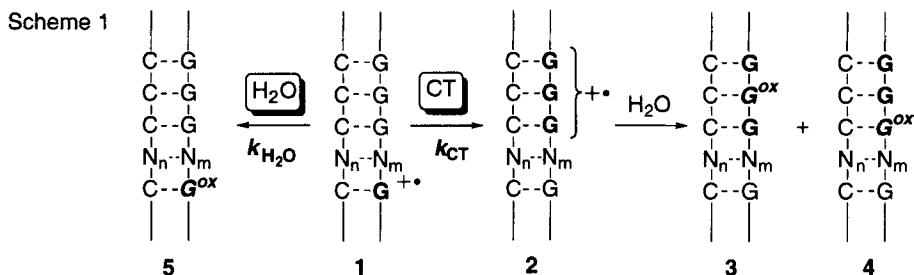
## HOLE TRANSPORT BETWEEN G BASES IN DNA

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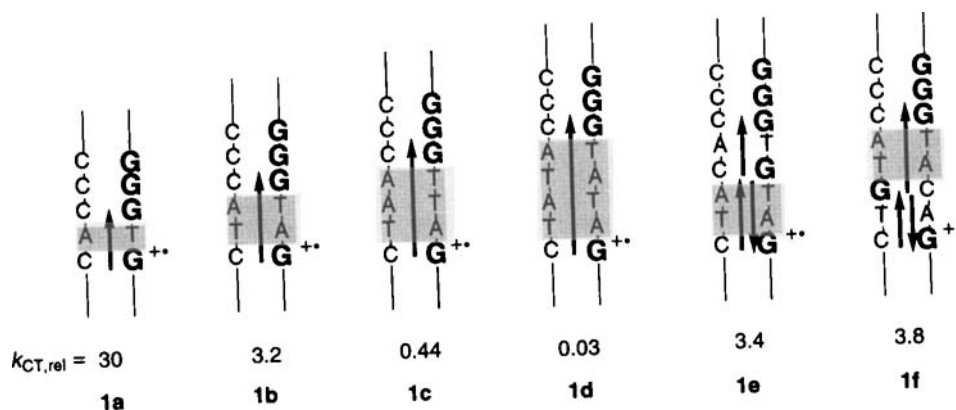
**ABSTRACT:** The mobility of positive charge in double stranded DNA was investigated. We found that long range hole transport efficiencies depend on the sequence and can be explained by a hole hopping process between G bases.

Recently, we have presented a new method to site selectively generate guanine radical cations ( $G^{\bullet+}$ ) in double stranded DNA by irradiation of 4'-pivaloyl modified oligonucleotides<sup>1</sup>. In order to address the mechanism of transfer of positive charge in DNA we have developed an assay which is based on the competition between charge transfer (CT) from a  $G^{\bullet+}$  to a GGG site and its trapping reaction with  $H_2O$  that generates an oxidized guanine ( $G^{ox}$ ) (Scheme 1)<sup>2</sup>. The amount of DNA strands that contain  $G^{ox}$  was determined by the piperidine method. The ratio of damage products (3+4)/5 is proportional to the ratio  $k_{CT}/k_{H_2O}$  and can be taken as a relative charge transfer rate  $k_{CT,rel}$ .



We analyzed the hole transfer between the G and GGG unit through one to four AT base pairs and obtained that  $k_{CT,rel}$  decreases by one order of magnitude with each intervening AT base pair (Scheme 2). This strong distance dependence led to a  $\beta$  value of  $0.7 \pm 0.1 \text{ \AA}^{-1}$  which is typical for hole transfer reactions via the superexchange mechanism. However, after exchanging the second or the third of the four AT base pairs in **1d** by a GC base pair, the rate of the hole transfer increased by two orders of magnitude (**1e,f**). This strong

increase in charge transfer efficiency cannot be explained with a single superexchange charge transfer step. Because  $G^{++}$  can oxidize G but not A bases, we suppose that the long range charge transport occurs via oxidation of the intervening G base. The one step charge transfer via a superexchange mechanism between  $G^{++}$  and GGG in double strands **1a-d** turns into a two step hopping process in double strands **1e,f**.



Scheme 2

A hopping mechanism could also explain hole transfer reactions over very long distances in mixed DNA strands if the GC pairs are separated from each other by only few AT base pairs. We have demonstrated this in an experiment with a double strand where the charge transport between  $G^{++}$  and the GGG unit takes place efficiently over 54 Å. For a situation in which the total charge transport over the distance  $\Delta r$  occurs in several hopping steps of the same distance  $\Delta r_{hop}$ , the theory of one dimensional random walk results in equation 1,

$$\ln(k/k_{hop}) = -2 \ln(\Delta r / \Delta r_{hop}) \quad (1)$$

where  $k$  and  $k_{hop}$  are the rate coefficients for the overall charge transport and the hopping steps, respectively. Equation 1 gives a weak, algebraic distance dependence of the overall charge transfer rate in a multistep hopping process. It is obvious that the exponential distance influence does not describe the long range hole transport in mixed sequences where a  $\beta$  value is not defined.

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#### REFERENCES

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