DNA Electron Transfer Through Partly Delocalized Bridge States: Enhancement of the Rate by Disorder

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OBJECTIVES

We seek for an explanation of a recent experiment [1] on hole transfer on a donor-acceptor-bridge system in DNA. A kinetic scheme of the experiment [1] is depicted in Figure 1. Holes are injected into a Guanine (G) and are transferred to a triple Guanine (GGG) either directly by tunneling or by thermal activation through the bridge. The transfer competes with a trapping reaction leading to products P_G and P_{GGG} that are measured. The challenge is to understand the almost absent distance dependence of the yield observed for long bridges in contrast with the N^{-1} distance dependence expected.

NEW RESULTS

A theory for electron transfer through a donor–bridge–acceptor system is presented which describes the tunneling and hopping–like transfer as well as the intermediate regime. The model includes a description of static and dynamic disorder in electronic energies and a delocalization of electronic states. A comparison of the theory with experimental data [1] on the relative yield P_{GGG}/P_G is shown in Figure 1. Exponential distance dependence of the relative yield is obtained for small bridge lengths $N < 3$, whereas an almost absent distance dependence is obtained for $N > 3$ in agreement with experiment. The theoretical curves were obtained for two different values of static disorder in site energies. Disorder decreases the exponentially dependent part of the yield whereas it enhances the yield for longer bridges ($N > 3$). A comparison of the present model with a standard model of nearest neighbor hopping is shown in Figure 2 for $N > 3$. The localized states hopping model reveals a steeper distance dependence and disorder decreases the yield.

CONCLUSIONS

The yield measured [1] for short bridge lengths reflects a superexchange transfer mechanism, whereas the flat distance dependence observed for longer bridges involves thermally populated states of the bridge. A nearest neighbor hopping model, within a reasonable range of parameters, does not explain the flat distance dependence observed for long bridges, whereas a description in terms of partly delocalized electronic states of the bridge provides an explanation. In the local state theory the disorder creates energetic barriers in the bridge which lead to a decrease of the rate with increasing distance. In the extended states theory the holes tunnel through such barriers. The enhancement of the yield with disorder in the extended states model is understood by considering how the local electron–vibrational coupling depends on the delocalization of electronic states.

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REFERENCES

1. B. Giese, J. Amaudrut, A.-K. Köhler, M. Spormann, S. Wessely, Nature, **412**, 318 (2001).

FIGURES

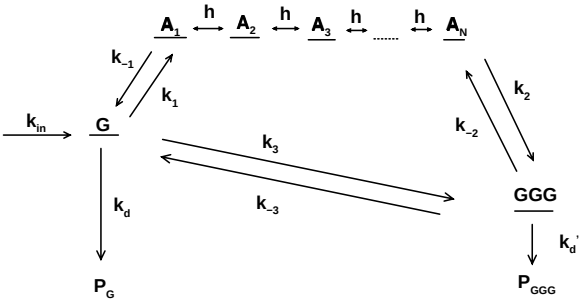

Figure 1. Kinetic scheme.

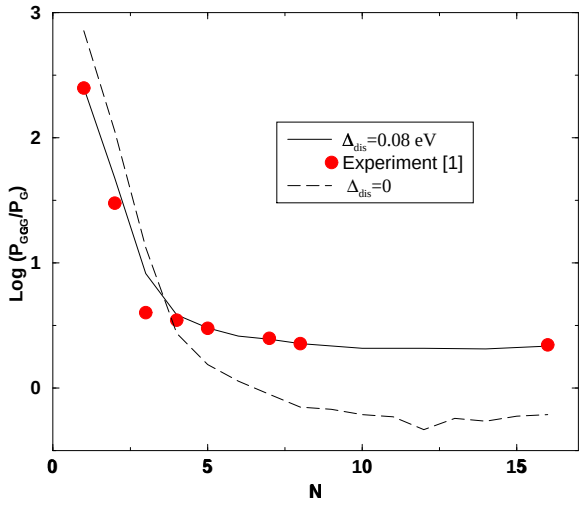

Figure 2. Relative yield of products in dependence on bridge lengths. Circles are the experimental values of ref. [1]. Δ_{dis} describes disorder in site energies.

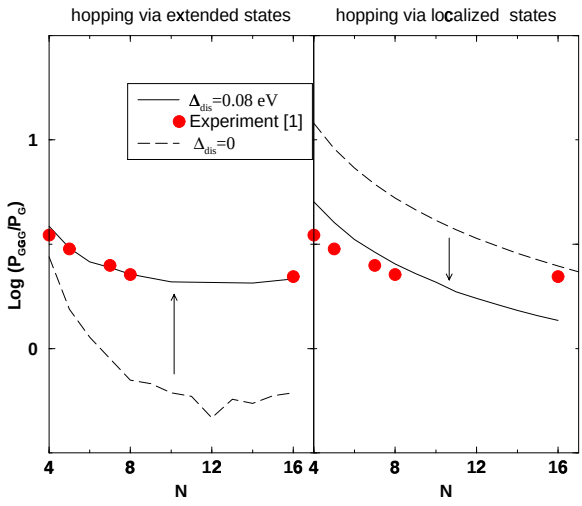

Figure 3. Comparison of nearest neighbor hopping

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