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Cytochrome oxidation in bacterial photosynthesis

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Abstract

In this paper we propose that the reduction of the bacteriochlorophyl dimer cation (P+ ) by cytochrome c in the photosynthetic bacteria Rps. viridis and Chromatium vinosum proceeds via two parallel electron transfer (ET) processes from two distinct cytochrome c molecules. The dominating ET process at high temperatures involves the activated oxidation of the high-potential cytochrome c at closest proximity to P, while the dominating low-temperature process involves activationless ET from a low-potential cytochrome c, which is further away from P. The available data for the effects of blocking the low-potential cytochrome c on ET dynamics are consistent with this model, which results in reasonable nuclear reorganization and electronic coupling parameters for the parallel cytochrome oxidation processes. The lack of universality in the cytochrome oxidation in reaction centres of various bacteria is emphasized.

Introduction

In 1989 the scientific world commemorates a hundred years since the discovery of the Arrhenius equation, which provides a conceptual framework for the quantitative description of the temperature dependence of chemical reactions in the homogeneous gas phase, in solution, in solids, in glasses and in biophysical systems. The temperature dependence of the rates of chemical reactions in a condensed medium is expected to exhibit serious deviations from the classical Arrhenius rate equation at low temperatures, where the effects of zero-point nuclear motion are manifest in tunneling effects. A multitude of chemical reactions, e.g., polymerization (Goldanskii 1986), proton transfer in solution (Siebrand et al. 1984), isomerization (Applebury et al. 1978) and group transfer in biophysical systems (Alberding et al. 1976), reveal low-temperature, temperature-independent rates, which originate from nuclear tunneling effects. Similar phenomena were predicted (Levich 1965, Kestner et al. 1974) for electron transfer (ET) in condensed phases; however, only recently some indication of nuclear tunneling on low-temperature ET rates in physico-chemical systems is emerging (Milosavljevic and Thomas 1986). In 1966 Don DeVault and Britton Chance (DeVault and Chance 1966) pioneered the exploration of low-temperature ET in biophysical systems, which manifests the breakdown of the Arrhenius equation due to nuclear tunneling phenomena. DeVault and Chance have discovered (DeVault and Chance 1966) a unique temperature dependence of the rate constant for the reduction of the bacteriochlorophyl dimer cation (P+ ) by cytochrome c in the photosynthetic bacterium Chromatium vinosum, at a low medium redox potential. The rate constant, k, for ET exhibits a sharp transition from a high-temperature activated region, where k drops by three orders of magnitude (i.e., from k = 10⁶ s⁻¹ at 298 K to k = 5 × 10² s⁻¹ at 120 K) to a temperature independent k at low temperatures (T < 120 K) (DeVault and Chance 1966, Dutton et al. 1971, Hales 1976, DeVault 1980). The characteristics of this reaction were attributed to the transition from temperature-independent nuclear tunneling at low temperatures to an activated process.
at high temperatures (Hopfield 1974, Jortner 1976, Kuznetsov et al. 1978, Sarai 1980, Buks et al. 1981, Dogonadze and Zakaraya 1987). Although such an interpretation is qualitatively plausible and appealing, the quantitative analysis of these experimental data in terms of multiphonon nonadiabatic ET theory raised serious conceptual difficulties. In order to obtain a good fit of the experimental data for *Chromatium* it is necessary to infer an unreasonably large nuclear reorganization energy at a high frequency, in conjunction with a very large electronic coupling (Bixon and Jortner 1986a, b, c). We have recently challenged (Bixon and Jortner 1986a, b, c) the traditional interpretation of the temperature dependence of the cytochrome oxidation reaction in *Chromatium*, which is attributed to ET from a single cytochrome *c* located at closest proximity to *P*⁺, to the dimer cation. Rather, we proposed (Bixon and Jortner 1986a, b, c) that in this photosynthetic bacterium two parallel ET processes from two distinct cytochrome *c* molecules to *P*⁺ take place. These involve:

1. An activated process, which dominates at high temperatures.

2. An activationless process, which is negligible at room temperature but is practically exclusive at low temperatures.

The structure and composition of the cytochrome *c* constituents of reaction centres exhibit large variations between different photosynthetic bacteria (Tiede et al. 1978, Chamorovsky et al. 1980, Rosen et al. 1983, Deisenhofer et al. 1984, 1985). At least for three bacteria, including *Chromatium vinosum* (Tiede et al. 1978) and *Rps. viridis* (Deisenhofer et al. 1984, 1985), it was shown that the reaction centre (RC) includes four cytochrome *c* molecules, which involve two high-potential and two low-potential cytochrome *c*. We originally suggested (Bixon and Jortner 1986a, b, c) that two distinct low-potential cytochrome *c* molecules are involved in the ET reactions (1) and (2). Recent experimental evidence for the RC of *Rps. viridis* identified the cytochrome *c* which is in closest proximity to *P* as a high-potential cytochrome *c* which is closest to *P*, and reaction (2) to ET from a low-potential cytochrome *c* (cytl) which is further away from *P*. We propose that this modified parallel cytochrome oxidation model is applicable for *Rps. viridis* for which the structure is established (Deisenhofer et al. 1985), and the spatial ordering of cyth and cytl can be deduced with high confidence (Dracheva et al. 1986, Shopes et al. 1987, G. Alegria and P. L. Dutton, personal communication), and presumably also for *Chromatium vinosum*.

The parallel cytochrome oxidation model which involves ET from cyth at high temperatures and from cytl at low temperatures provides an interesting mechanistic prediction. Blocking of the cytl, which can be accomplished by maintaining it in the cytl⁻³ oxidized form, will close the effective low-temperature channel. Accordingly, the low-temperature ET rate to *P*⁺ at a moderate medium redox potential, where the initial state is *P*⁺cyth⁻²cytl⁻³, will be drastically lower than the rate at a low medium redox potential, where the initial state corresponds to *P*⁺cyth⁻²cytl⁻². On the other hand, the high-temperature ET rates at moderate and at low medium redox potentials are expected to be similar. This prediction is borne out by the available experimental data for cytochrome(s) oxidation in *Rps. viridis*. The high-temperature rates at 298 K are $k = 3.7 \times 10^6$ s⁻¹ at a moderate medium redox potential (Dracheva et al. 1986, Shopes et al. 1987), and $k = 7 \times 10^6$ s⁻¹ at a low medium redox potential (Shopes et al. 1987). In contrast, the low-temperature rates are drastically different for these two situations, being $k = 10^8$ s⁻¹ at 77 K for the low medium redox potential (Chance et al. 1969), corresponding to ET from P⁺cyth⁻²cytl⁻², and $k = 3.6 \times 10^2$ s⁻¹ at 125 K for the moderate medium redox potential (Shopes et al. 1987), which corresponds to ET from P⁺cyth⁻²cytl⁻³. The three orders of magnitude decrease of the ET rate from P⁺cyth⁻²cytl⁻³ relative to the ET rate from P⁺cyth⁻²cytl⁻² at low temperatures reflects the blocking of the parallel ET channel which is dominant at low temperatures.

In this paper we apply the parallel model for cytochrome oxidation to the reaction centres of *Rps. viridis* and of *Chromatium*. For *Rps. viridis* our analysis provides some predictions regarding the detailed temperature dependence of this process, which has not yet been explored. The resulting reorganization and electronic parameters resulting