ON ELECTRON TRANSFER

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ABSTRACT The tunneling transfer of electrons between two sites, appropriate to biological intermolecular electron transfer, contains physical considerations which are not important in the tunneling transfer between two metals. Analyses (such as the recent one by Hales) based on the well-known formula for the latter but applied to the former case are quantitatively and qualitatively misleading.

Contrary to the example of grammatical usage, error in science does not become correct through repetition. The recent paper in this journal by Hales (1) is based entirely on the erroneous supposition that the rate of transfer of electrons between a pair of sites can be written as:

$$t_{1/2} \propto [V^2/E^2(V - E)]\, e^{2W_t\,[2m(V-E)^{1/2}/\hbar]},$$

where $t_{1/2}$ is the halftime for crossing the barrier, V the barrier height, W_t the barrier width, m the electron mass, and E the energy of the electron. This oft-quoted expression is both conceptually wrong and quantitatively misleading when applied to electron transfer between two molecules. The formula applies to a situation in which a continuum of free electronic states is available for the final electron and provides the essential density of states for making transitions. The formula is meaningless when applied to a case in which the final state is one particular (localized) electronic level. It does not contain the mechanism (vibronic coupling) by which energy is conserved (and a density-of-states is obtained) in the case to which it is being applied. Its "application" in the case at hand explicitly violates the conservation of energy. The discussion of this subject is already in the literature (2).

Hales apparently rejects vibronic coupling ideas because they often (but not invariably) lead to electron transfer distances of 5–10 Å rather than 30 Å scale. However, small molecules exchange electrons with cytochrome *c* via the almost exposed heme edge, rather than through 20 Å of protein (3). Electron exchange between the α- and β-hemes of hemoglobin (one oxidized, one reduced) which are separated by 25 Å (Fe-Fe distances) takes days (4) and is probably accomplished by mediators or

heme exchange, rather than by direct electron transfer. Direct evidence for long range transfers in biological systems is chiefly lacking.

To reject the vibronic coupling description because it leads to relatively short transfer distances seems a distorted (though perhaps tenable) view of available information on transfer distances. But to use instead the above equation is to favor alchemy over chemistry.

The thesis of Hales, that a temperature-dependent width or height of a tunneling barrier makes a significant contribution to the temperature dependence of transfer rates, may of course turn out to be correct in spite of the inadequacy of the analysis thus far provided.

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