In Quest of a Simultaneous Two Electron Transfer: Does a Simultaneous Two-Electron Transfer Occur in Organic (Electron Transfer) Reactions?

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Sir,

Frequently we come across in the literature with the electron transfer reactions represented by

$$Ox + ne \rightleftharpoons R \quad (1)$$

or

$$Ox + ne \rightarrow R \quad (2)$$

Where $n > 1$.

If the reaction (1) or (2) represents an overall picture involving several steps, well and good. However, occasionally, reports do appear where workers[1-2] have claimed to observe n = 2 (eq. 1) in a single step! There is one example (for duroquinone) where the transfer of electron is associated with a transfer of two counterions[4].

We are exploring the existence of a simultaneous two-electron transfer in organic systems[5] and we present experimental evidences based on which we question such claims made about the occurance of a simultaneous two-electron transfer. Such claims made by workers from time to time must be entertained with caution because these claims may be erroneous and alterantive mechanism may be available to explain the same observation (*loc cit.*).

Evidences are as follows:

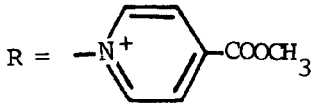
(a) The exchange

$$\phi_2C{:}\ C\phi_2 + \phi_2C^{-}.\ C\text{-}\phi_2,\ 2Li^{+} \rightarrow \text{Exchange}$$

(where $\phi_2C{:}\ C\phi_2$ is tetraphenyl ethylene) studies has only given the upper limit of the rate constant[5]. It is also possible that the rate constant is zero.

(b) The polarographic and cyclic voltammetric reduction of such dications as

$$R - (CH_2)_n - R + n_e e \rightleftharpoons;\ n = 2,3,4$$



always give the value $n_e=1$ (n_e = number of electron involved in reactions process) from the analysis of the wave[6].

(c) Reduction of methyl viologen dichloride also gave the value $n_e=1$ and mono-cation radical is produced[7].

(d) Reduction of dinitrobibenzyl as carried out cyclic voltammetrically[8] gives a wave which gives $n_e=1$.

(e) Electron exchange between cyclo-octatetraene, as studied by proton NMR (in tetrahydrofuran and diethyl ether solvents) showed the absence of simultaneous two electron transfer[8].

(f) A high disproportionation

$$2R \rightleftharpoons R^{\cdot} + Ox \quad (3)$$

where

$$Ox + e \rightleftharpoons R \quad (4)$$

$$R + e \rightleftharpoons R^{-} \quad (5)$$

could wrongly be interpreted as a simultaneous two electron transfer[8(c)].

Thus heterogeneous (electrochemical)as well as homogeneous electron transfer is expected to occur, has given every indication that a simultaneous two electron

transfer does not occur.

Argument could be advanced that the geometry of the donors and acceptors, in the above cases studied, may not be favourable, at the time of electron transfer[5,8(b)]. Thus, even in the case of heterogeneous electron transfer (electrochemical reduction), it may be said that only one acceptor site is in the double layer facing the electrode. A study varying *n* (number of ethylene group) in dipyridinium salts (B), still showed that the number of electron involved in the reduction process is unity. A final test of effect of geometry on the two electron transfer may be made in the system like 1,2 diphenyl cyclohexene-1 dianion and its parent hydrocarbon[9]. The reason being that, most probably, both species will be of almost identical geometry.

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