

## Application of Symmetry Correlations to Homogeneous Chemiluminescent Electron Transfer Reactions

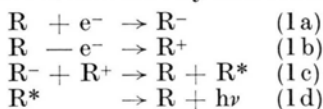
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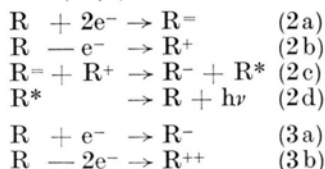
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Chemiluminescent redox reactions,  
Symmetry correlations

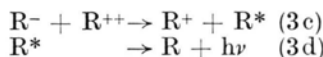
Light emission accompanying homogeneous electron transfer reactions between electrochemically produced anionic and cationic radicals of aromatic hydrocarbons in nonaqueous solvents (reaction (1)) has been the subject of numerous investigations in recent years. Interest in this area began with three reports<sup>1</sup> in which HERCULES and CHANDROSS *et al.* independently observed light emission in the vicinity of solid electrodes upon alternating current electrolysis of aromatic hydrocarbons.



The proposed mechanism for this type of reaction was the initial transfer of an electron from the singly occupied antibonding molecular orbital of the anion to the unoccupied antibonding molecular orbital of the cation, followed by an intramolecular radiative emission from the excited hydrocarbon thus produced. MARCUS<sup>2</sup> treated the electrochemiluminescence phenomenon theoretically, using his general equation for electron transfer reactions and concluded that the emissive pathway was a reasonable one for the removal of excess energy in these exothermic reactions. Some examples of this type of redox reactions have been presented and reviewed<sup>3</sup> and work on the properties of these and new systems is continuing. For example, in a recent study<sup>4</sup> it was observed that the reactions involving dianions and dicationic of the same systems (reactions (2) and (3)) are also capable of producing excited states, provided that the dianion or dication is sufficiently stable during the experiment. In reaction (2c) (similar to the



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case in reaction (1c)) the electron transfer occurs from the doubly occupied antibonding molecular orbital of the dianion to the unoccupied molecular orbital of the cation, whereas in reaction (3c) the electron transfer must be from the highest occupied bonding molecular orbital of the anion to the unoccupied bonding orbital of the dication (Fig. 1).

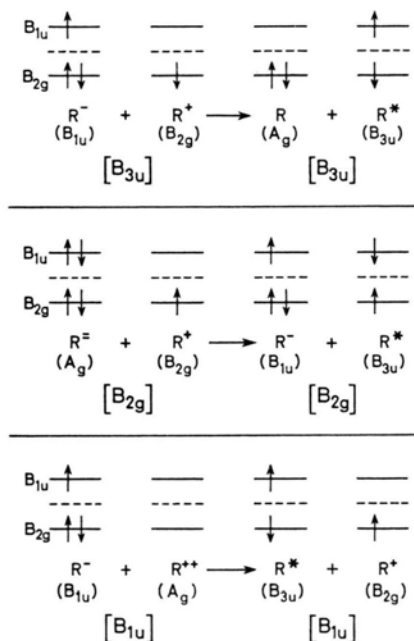


Fig. 1. Molecular orbitals and symmetry representations of the emissive pathways in electron transfer reactions of aromatic hydrocarbon radical ions of anthracene.

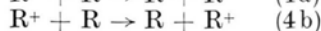
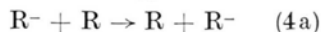
The importance of symmetry considerations in predicting the route and the nature of the products of some concerted chemical reactions<sup>5</sup> has attracted considerable attention among chemists. In those reactions to which the group theoretical correlations are applied, some chemical bonds are broken and some new bonds are formed. In spite of such complexities, the symmetry rules have successfully predicted the fate of these reactions. In electron transfer reactions of the type discussed above, no bonds are broken and no new bonds are formed. It should therefore be expected that symmetry rules can be more easily applied to these simple cases.

If we represent the wave function of the reactants as  $\Psi_R$  and that of the products as  $\Psi_P$ , these two must belong to the same irreducible representation of the point group of the molecule in order for a certain reaction to occur. The physical meaning of this is that the two wave functions must overlap in a nonvanishing manner. Let us now analyze reactions (1c, 2c and 3c) for a typical electrochemi-

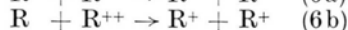
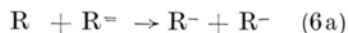
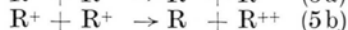
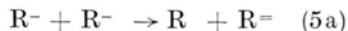
luminescent system such as anthracene. This molecule belongs to  $D_{2h}$  point group. The symmetry representations of all the species involved in the electron transfer reactions are given in Fig. 1. For reaction (1c),  $\Psi_R$  has a symmetry of  $B_{1u} \times B_{2g} = B_{3u}$  and  $\Psi_P$  has a symmetry of  $A_g \times B_{3u} = B_{3u}$ , so that the initial and the final wave functions belong to the same irreducible representation of this point group. Therefore, the production of one of the neutral molecules in an excited state is an allowed process both thermodynamically and by symmetry. The production of both the molecules in the ground state ( $R^+ + R^- \rightarrow R + R$ ) (which is also thermodynamically allowed process) would be symmetry forbidden. In the latter case the product wave function has  $A_g \times A_g = A_g$  symmetry which does not match up with  $B_{3u}$  symmetry of the wave function of the reactants. This nonemittive pathway should not have a significant probability in the overall reaction mechanism. When the same simple procedure is carried out for reactions (2c and 3c), it is seen (Fig. 1) that for these processes also, the only symmetry allowed route is the one which generates a neutral molecule in an excited state.

Chemiluminescent anion-cation annihilation re-

actions of the above type; simple electron exchange reactions of type



and certain disproportionation or reproporation reactions of type



are all known to be extremely fast bimolecular reactions whose rate constants<sup>3b,6</sup> are of the order of  $\sim 10^6$ – $10^9$  l · mole<sup>-1</sup>. Such large rate constants in all these cases, as well as the production of excited species in reactions (1c, 2c and 3c), are the natural consequence of the conservation of symmetry.

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