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On the Theory of Chemiluminescent Electron-Transfer Reactions*

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A mechanism is described for chemiluminescent electron-transfer reactions. It is shown that in the case of very exothermic homogeneous electron-transfer reactions, the intersection of the potential-energy surface of the reactants with that of electronically unexcited products occurs only at high energies. The rate of formation of unexcited products then becomes slow. A numerical estimate of this slowness is made using known homogeneous rate constants for ordinary electron-exchange reactions. An intersection occurs at lower energies when one of the products of a highly exothermic electron transfer is electronically excited, thereby reducing the exothermicity. The product may emit light or subsequently form a state that does.

A rather different situation is shown to occur at electrodes: the system can now reduce the "exothermicity" by having the electron transfer into a high unoccupied level of the conduction band or from a low occupied level of the latter. The large width of the conduction band in metals permits much latitude in reducing the exothermicity thereby.

These results are compared with present experimental findings that chemiluminescent electron transfers occur in solution rather than on electrode surfaces.

A VARIETY of atom-transfer chemiluminescent reactions are known, but more recently a number of chemiluminescent electron-transfer reactions have been reported in the literature.[1a–d] We apply a theory of electron transfers[2] to these reactions and examine some consequences for experiment.

We consider a potential-energy surface for the reactants and one for the products, each plotted as a function of all the translational, rotational, and vibrational coordinates in the system.[2] In the zeroth approximation of no electronic coupling of the redox orbitals of the ion and electrode, these two potential-energy surfaces intersect. In the next approximation of some electronic coupling, the intersection is removed by the usual quantum-mechanical splitting, as in Fig. 1(a). A suitable fluctuation of coordinates involving approach of the reactants, reorientation of solvent molecules, and change in bond lengths of reactants, permits the system to cross the original intersection region in a coordinate region (small separation distance) where the electronic coupling is appreciable. In this way electron transfer has occurred, adiabatically if the splitting is sufficient and nonadiabatically otherwise. The system has moved from the R to the P surface [Fig. 1(a)].

In the usual thermal electron-transfer reaction, the products are formed in their electronic ground states, for only these are usually conveniently accessible energetically. Nevertheless, the potential-energy surface of the reactants will "cross" a surface of the products in which one or more products is electronically excited, in some other region of configuration space. If this latter intersection region is easily accessible (energetically and entropically), a reaction to form an excited product can occur. The excited product may either emit light or react. An example of such a reaction is a possible triplet–triplet annihilation to form an excited singlet state which later fluoresces.[1e]

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[1] (a) D. M. Hercules, Science **145**, 808 (1964); (b) E. A. Chandross and F. I. Sonntag, J. Am. Chem. Soc. **86**, 3179 (1964), and references contained therein; (c) K. S. V. Santhanan and A. J. Bard, *ibid.* **87**, 139 (1965); (d) G. J. Hoitjink (private communication); (e) This possibility was suggested to the writer by G. J. Hoitjink: In some cases, polarographic data on aromatic compounds suggest that a reaction may be sufficiently exothermic to form a triplet state of an aromatic molecule but not quite enough to form an excited singlet. The triplets may then phosphoresce in rigid media, or in solution they may annihilate each other or react with other solutes. Polarographic data are summarized by G. J. Hoijtink, Ind. Chim. Belge **12**, 1371 (1963).

[2] (a) R. A. Marcus, Ann. Rev. Phys. Chem. **15**, 155 (1964) and references cited therein; J. Chem. Phys. **43**, 679 (1965); (b) Discussions Faraday Soc. **29**, 21 (1960); (c) J. Phys. Chem. **67**, 853, 2889 (1963).

In a sufficiently exothermic[3] electron-transfer reaction the region where the surface of unexcited products "intersects" that of unexcited reactants is not readily accessible and becomes less accessible with increasing exothermicity.[4] Under such conditions the region where the potential-energy surface involving an excited product intersects that for the unexcited reactants may be readily accessible. The formation of an excited product can then occur easily.

A numerical estimate of the rate to form an unexcited or an excited product can be made as follows: The electron-transfer rate constant k to form a particular electronic state of the products is given by (1), according to an electron-transfer theory[2a]:

$$k=Z\kappa\rho\exp(-\Delta F^{*}/kT), \tag{1}$$

where Z is about 10^{11} liter $\text{mole}^{-1}\cdot\text{sec}^{-1}$, κ is a factor close to unity unless the splitting is extremely small, $\rho\sim1$, and ΔF^{*} reflects the accessibility of the intersection region:

$$\Delta F^{*}=w^{r}+(\lambda/4)[1+(\Delta F_{R}^{o\prime}/\lambda)]^{2}, \tag{2}$$

$$\Delta F_{R}^{o\prime}=\Delta F^{o\prime}+w^{p}-w^{r}. \tag{3}$$

In these equations w^{r} is the work required to bring the reactants together to the most probable separation distance R in the intersection region, i.e., in the "activated complex"; w^{p} is the corresponding work to bring the products together, each w referring to the given state of excitation. $\Delta F^{o\prime}$ is the "standard" free energy of reaction in the prevailing medium. λ is a reorganization term, expressible in terms of differences in equilibrium bond lengths of each reacting species in its initial and final electronic states[5] and in terms of dielectric properties related to differences in equilibrium orientation polarization in these electronic states.

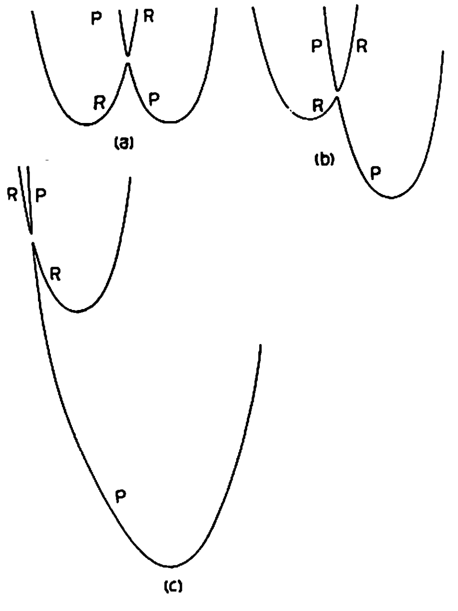

FIG. 1. Profile of potential-energy surface of reactants (R) and that of products (P) plotted versus configuration of all the atoms in the system. The adiabatic surfaces are indicated by solid lines for the case of (a) $\Delta F^{o\prime}\cong0$, (b) $\Delta F^{o\prime}<0$, and (c) $\Delta F^{o\prime}\ll0$.

Equation (2) displays an interesting behavior as $\Delta F^{o\prime}$ becomes increasingly negative for a reaction leading to the given[5] electronic state of the products. At small $\Delta F^{o\prime}$ the "barrier" ΔF^{*} decreases with increasingly negative $\Delta F^{o\prime}$, the expected slope of 0.5 being supported by recent experimental studies.[6] In this region of $\Delta F^{o\prime}$, a typical region in fact for chemical reactions, the likely configurations of coordinates at the intersection region represent some compromise between stable coordinate configurations of the reactants and those of the products [Figs. 1(a) and (b)].[2]

When $\Delta F^{o\prime}$ becomes so negative that it equals λ (neglecting the work terms w^{r} and w^{p} for the moment) ΔF^{*} vanishes. For still more negative $\Delta F^{o\prime}$'s, ΔF^{*} begins to increase with increasingly negative $\Delta F^{o\prime}$, as one sees from Eq. (2). In this new $\Delta F^{o\prime}$ region the intersection region does not occur at compromise configurations [Fig. 1(c)]. With increasingly negative $\Delta F^{o\prime}$ the intersection's configurations become increasingly different from both the stable configurations of the reactants and those of products for the given electronic states [Fig. 1(c)]. The above $\Delta F^{0\prime}$ regions can be called the "normal" and "abnormal" $\Delta F^{0\prime}$ regions.

When the value of λ for reaction leading to a ground state and for that leading to an excited state is about the same, the difference of ΔF^{*}'s for the two reactions is determined by the respective values of $\Delta F^{o\prime}/\lambda$ [Eq. (2)]. The magnitude $\Delta F^{0\prime}/\lambda$ for a typical reaction of interest can be determined as follows: We consider a reaction leading to an excited state for which the excitation energy is about 3 eV. (The calculations are easily amended for a different excitation energy.) As a first approximation (neglecting $T\Delta S^{o\prime}$) the $-\Delta F^{o\prime}$ for the ground-state reaction is then about -70 kcal mole^{-1}.

The value of λ can be estimated from appropriate homogeneous or electrochemical electron-transfer rates of related reactions when they are available.[2] For example, the λ appearing in (1) is essentially the mean of the λ's of the two electron-exchange reactions (4) and (5),[2]

$$\mathrm{A_{ox}+A_{red}\rightarrow A_{red}+A_{ox}}, \tag{4}$$

$$\mathrm{B_{ox}+B_{red}\rightarrow B_{red}+B_{ox}}, \tag{5}$$

for the cited electronic states. That is, λ_{ab} equals $\frac{1}{2}(\lambda_{aa}+\lambda_{bb})$. Alternatively, if λ_{aa}^{el} denotes the λ for the electrochemical exchange rate the theoretical λ_{aa}^{el}

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[3] In the present paper we use the word "exothermic" for convenience to designate a reaction with a large negative standard free energy of reaction rather than specifically one with a large negative heat of reaction. However, for these reactions $|T\Delta S^{o}|\ll|\Delta H^{o}|$ normally.

[4] See Ref. 2(b), where the postulated effect was called an inverted chemical effect.

[5] That is electronic states shortly prior to and after electron transfer.

[6] For example, R. J. Campion, N. Purdie, and N. Sutin, Inorg. Chem. 3, 1091 (1964), and references cited therein.

equals $\lambda_{aa}/2$ essentially, and λ_{ab} equals $\lambda_{aa}^{el}+\lambda_{bb}^{el}$.[7] (We restrict our considerations to systems in which adsorption at an electrode is absent.) Evidence supporting these ideas has been given recently.[2a,c]

When A_{red} is an aromatic anion and A_{ox} an aromatic molecule, an estimate of λ can be made from available measurements of the reaction rate constant for (4). The value of k is about 10^7-10^9 liter $mole^{-1}\cdot sec^{-1}$.[8] (However, the results are complicated by at least partial alkali cation bridging. Certain peculiar factors suggest that further study of the mechanism is desirable.[9]) Analogous data without cation bridging are available for another aromatic compound, Wurster's blue and its positive ion, for which k is about 10^8 liter $mole^{-1}\cdot sec^{-1}$.[10] If work terms are neglected for simplicity and if these data provide a rough measure of k for an unbridged reaction then $\lambda_{aa}/4$ is about 4 kcal $mole^{-1}$ for an aromatic system, a very small value.

The value of λ_{bb} depends on the nature of B. When λ_{bb} is also small, roughly equal to λ_{aa}, then $\lambda/4$ becomes about 4 kcal $mole^{-1}$ and $-\Delta F^{o\prime}/\lambda$ becomes about 4.4. The barrier ΔF^* leading to an unexcited product then equals $3.4\lambda/4$ kcal $mole^{-1}$ according to (2). Such a reaction has a rate constant which is extremely small, the reaction proceeding only at one in every 10^{10} collisions.

On the other hand, for this small λ, the reaction leading to formation of an excited state occurs with a high rate if that state of the products is accessible. For example, according to whether $\Delta F^{o\prime}$ for formation of an excited state is 0 or -10 kcal $mole^{-1}$, assumption of the same λ yields a ΔF^* of $\frac{1}{4}\lambda$ or $\frac{9}{64}(\frac{1}{4}\lambda)$, respectively. The reaction then proceeds at one in every 10^3 or one in every three collisions, respectively.

As calculations based on (2) readily verify, a large difference in rates leading to formation of an excited state vs ground state of a product, and favoring the former, exists for this very exothermic system even for larger λ_{bb}'s, though not for very large λ_{bb}'s. It should be noted, however, that λ for an elementary step depends on the change of equilibrium bond lengths of each reacting species in that step, and so may differ in the two competitive reactions. Knowledge of the electronic states often permits an at least qualitative insight into these differences in the absence of exact quantitative calculations.

By introduction of suitable substituents in the aromatic ring, some manipulation of the $\Delta F^{o\prime}$'s becomes possible, making formation of an excited state difficult or easy and suggesting thereby further experiments. Extensive variation of $\Delta F^{o\prime}$ of inorganic complexes containing heterocyclic aromatic ligands has been achieved in this way for ordinary electron-transfer reactions.[6] Under suitable conditions the $\Delta F^{o\prime}$'s for ground-electronic-state reactions are available from polarographic half-wave potentials, even for some electrochemically irreversible systems.

The above remarks apply to homogeneous electron-transfer reactions. The mechanism of electrochemical electron transfers can also be analyzed in terms of motion on potential-energy surfaces.[2] A major difference now arises, however: For any electronic state of the reactant there are many potential-energy surfaces, each shifted vertically from one another and each involving a different many-electron quantum state of the electrode. In terms of one-electron states, each many-electron state corresponds to a different distribution of electrons of the metal among one-electron states. Thus, the surface R in Fig. 1 now denotes one of these many surfaces for the given electronic state of the reactant and for a given many-electron state of the electrode. Similarly, the surface P in Fig. 1(a) now denotes a surface for the given electronic state of the product and that of the electrode.

The splitting at the intersection of an R and P surface depends on the particular surfaces, varying from zero to an appreciable amount: In terms of one-electron quantum states of the electrode, there is an appreciable splitting at an "intersection" of an R and P surface for a one-electron transfer if the distribution of electrons among the one-electron quantum states is the same for the given R and P states except for the electron undergoing transfer. We term such a pair of surfaces as suitable for occurrence of electron transfer.

Although there is now almost a continuum of such R and P surfaces, most electron transfers under the usual electrochemical conditions occur to and from one-electron electrode quantum states which are within kT of the Fermi level[2a]: in the case of electron transfer from ion to electrode, transfer to a suitable but high P surface is unlikely because of the greater activation energy needed to reach the intersection region. Transfer to a low P surface is difficult because the probability of finding an otherwise suitable surface having an unoccupied one-electron orbital is small. Most of the one-electron states that are more than kT below the Fermi level are already occupied. A quantitative description has been given elsewhere.[2a]

An equation derived for the electrochemical rate constant is given by (1),[2] where Z is now about 10^4 cm sec^{-1}, λ is the electrochemical λ, which has a value of about one-half the value of λ for a homogeneous electron-exchange reaction such as (4),[2,7] and $\Delta F^{o\prime}$ is replaced by $ne(E-E_o')$. n is the number of electrons transferred, usually equal to one in an elementary

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[7] When λ is very small, λ may arise largely from change in orientation polarization and so be more sensitive to specific influences. $\lambda_{el}=\frac{1}{2}\lambda_{ex}$ if the mean separation distance of the reactants in the activated complex of the exchange reaction equals the distance between the ion and its electrostatic image in the electrode reaction, and if specific effects affect the λ's but slightly.

[8] (a) R. L. Ward and S. I. Weissman, J. Am. Chem. Soc. **79**, 2086 (1957); (b) P. J. Zandstra and S. I. Weissman, *ibid.* **84**, 4408 (1962); (c) T. Layoff, T. Miller, R. N. Adams, H. Fah, A. Horsfield, and W. Proctor, Nature, **205**, 382 (1965).

[9] For example, Ref. 2(b), the activation energies are anomalously high, considering the high rate constants. As a result, the frequency factors A for the apparent cation-free path are too high by many orders of magnitude: $A=10^{17}$, 10^{17}, and 10^{23} liter $mole^{-1}\cdot sec^{-1}$ naphthalene–naphthalene anion in three solvents, rather than the expected 10^{11} liter $mole^{-1}\cdot sec^{-1}$ or somewhat less.

[10] A. D. Britt, J. Chem. Phys. **41**, 3069 (1964).

step. E and E_o' are the electrode–solution potential and the "standard" electrode–solution potential drop for the given elementary step involving the given electronic states of reactant and product.

We consider now a very exothermic[3] electrode process involving transfer of an electron from the ion to the electrode, i.e., a process that would be very exothermic if transfer occurred to the Fermi level of the electrode. There are now many suitable potential-energy P surfaces that cross the original R surface at an accessible region, and each corresponds to the electron going into some high unoccupied orbital of the metal, near the top of the unfilled half of the conduction band if need be. Because of the large width of this band in metals[11] the system can easily reduce the exothermicity, by electron transfer into such an unfilled level.

Similar remarks apply to a very exothermic electron transfer from an electrode to a molecule or ion in solution. In this case the electron can relieve the exothermicity by coming from one of the lower levels in the filled half of the conduction band.

Even when the exothermicity for transfer to or from the Fermi level is of the order of 3 eV it can be alleviated[12] because the widths of the unfilled and filled halves of the conduction band are each at least this amount.[11] Transfer then proceeds to or from one-electron states in the electrode for which the ΔF^* in Eq. (2) is small, in the case of adiabatic transfers. [The $e(E-E_o')$ which replaces ΔF^o there for a one-electron-transfer electrode reaction is in turn now replaced by $e(E-E_o')\pm(\epsilon-\epsilon_F)$, where $\epsilon-\epsilon_F$ is the energy of this one-electron quantum state in the metal relative to that of the Fermi level. The sign depends on the convention used for E_o'.]

Thus, unless the formation of the excited state of an ion by electron transfer to or from the electrode has a very small ΔF^*, it cannot compete with the above process which involves formation of the ground state of an ion and an excited state of the electrode.

In agreement with these observations, no chemiluminescence has been observed when an aromatic anion comes in contact with a positively charged metal electrode.[1d] Again, when an aromatic anion is formed at an electrode and the electrode is suddenly made very positive[1a,c] no chemiluminescence occurs until the supporting electrolyte is oxidized by the electrode. A homogeneous chemiluminescent reaction between the aromatic anion and the resulting radicals was then presumed to occur.

It would be interesting to investigate theoretically and experimentally the possibility of chemiluminescence with electrodes for which the conduction band width is small. Semiconductor electrodes offer such a possibility. Electron-transfer theory has been applied to these electrodes.[13] The fact that transfer can occur with both the valence and conduction bands would, of course, be taken into consideration.

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[11] This width of the filled half of the conduction band is about 3.7, 5.8, 7.1, 4.2, and 3.0 eV for Fe, Ni, Cu, Li, and Na, respectively. See soft x-ray emission studies of E. M. Gyorgy and G. G. Harvey, Phys. Rev. 93, 365 (1954), and of S. Raimes, Phil. Mag. [7] 45, 727 (1954); cf. D. Pines, Solid State Phys. 1, 368 (1955); C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1961), 2nd ed., p. 310.

[12] An example where the exothermicity is not alleviated occurs in the neutralization of gaseous He^+ by metal electrodes. Here, the exothermicity is the difference between the ionization potential (24.47 eV) and the work function of, say a molybdenum electrode (4.3 eV). It is extremely large. On the other hand, the difference between the "ionization potential" of the 2^3S excited state of helium (4.5 eV) and this work function is very small. Thereby, helium atoms are formed in metastable states. See H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Oxford University Press, London, 1952), p. 570 ff.

[13] Compare the theoretical studies of electrode reactions by Levich, Dogonadze, and Chizmadzev and by Gerischer, described or noted in Ref. 2(a). Electron transfers at semiconductor electrodes have also been discussed by these authors, and by Dewald.[2a]