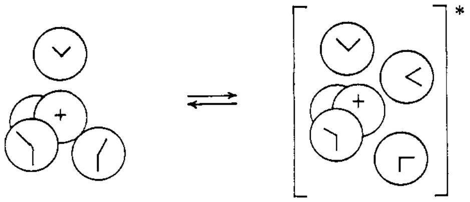

Figure 1. Reactant and transition state structures for conductance of an alkali metal ion in aqueous solution.

in the transition state in contrast to four in the reactant state, the correspondingly stronger bonding to each at the transition state should lead to an increased librational frequency. The restriction to rotation, due to ion–dipole attraction or hydrogen bonds, is primarily electrical, because even with four attached the surrounding water structure is open and uncrowded. The fact that the calculated average librational frequency for the solvating waters *drops* for all these ions (*cf.* Table V for $n^* = 3$) seems to exclude this mechanism. On the other hand, if the addition–elimination mechanism is correct and a larger number of water molecules is attached at the transition state, the bonding to each should be weaker and the frequency should drop, as calculated (*cf.* Table V for $n^* = 5$). This looser bonding in the transition state can also be viewed as resulting in formation of free volume around the ion, which allows the ion to move through the solution in small discrete steps. In summary, the migration of an alkali or halide ion through water is a process involving making and breaking solvation bonds to the ion. The coordinated water molecules at the transition state are each more loosely bound than those of the reactant, whether one assumes three, four, or five. This seems unreasonable for three (initial decrease in number of solvating water molecules), but consistent with prior or incipient coordination of an *additional* water (Figure 1).

Theory of Controlled Potential Electrogeneration of Chemiluminescence[1]

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Abstract: Several workers have reported chemiluminescence produced by electrogeneration at a single electrode of anion and cation radicals of a large number of aromatic hydrocarbons. Light emission probably results from a radical-annihilation reaction, followed by radiative decay: (1) $R^+ + R^- \xrightarrow{k} R + R^*$; (2) $R^* \rightarrow R + h\nu$. The purpose of this paper is to relate quantitatively the light intensity produced in electrogenerated chemiluminescence to the current, time, and kinetic parameters. These relationships have been calculated for a double potential step mode of generation. In a solution containing only the organic species R, the electrode potential is initially set so that zero current flows. A sufficiently positive potential pulse of duration t_f is applied to the electrode so that the concentration of species R at the electrode surface instantaneously becomes zero as R is oxidized to the cation radical R^+. The positive pulse is immediately followed by a negative potential pulse of duration t_r so that the surface concentrations of both species R and R^+ are zero as the anion radical R^- is generated. During the negative pulse the annihilation and light emission reactions (see above) occur in the diffusion layer. The calculations are made using an IBM 7094 digital computer.

Hoijtink and co-workers[2] were the first to report chemiluminescence resulting from the reaction between the cation and anion radicals of anthracene. Subsequently, several workers have produced chemiluminescence by the electrogeneration of the anion and cation radicals of various organic aromatics at a single electrode surface using alternating current[3] and alternating potential techniques.[4]

Nearly all workers have suggested the formation of an excited singlet state, which undergoes radiative and nonradiative decay to the ground state. The following generalized mechanism may be written

$$R \longrightarrow R^+ + e^- \qquad \text{oxidation at electrode surface} \qquad (1)$$

$$\left.\begin{array}{l} e^- + R \longrightarrow R^- \qquad (2) \\ 2e^- + R^+ \longrightarrow R^- \qquad (3) \end{array}\right\} \text{reduction at electrode surface}$$

$$R^+ + R^- \xrightarrow{k_4} R^* + R \qquad \text{in bulk of solution} \qquad (4)$$

$$R^* \xrightarrow{k_5} R + h\nu \qquad \text{radiative decay} \qquad (5)$$

$$R^* \xrightarrow{k_6} R \qquad \text{nonradiative decay} \qquad (6)$$

$$R + R^* \xrightarrow{k_7} 2R \qquad \text{self-quenching} \qquad (7)$$

where R is the organic molecule, R^+ and R^- are the cation and anion radicals, and R^* is the molecule in the excited state. Chandross, Longworth, and Visco[5]

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[1] This work was performed under the auspices of the U. S. Atomic Energy Commission.

[2] Private communication by Professor Hoijtink to E. A. Chandross and F. I. Sonntag, Bell Telephone Laboratories, Inc., Murray Hill, N. J.; see E. A. Chandross and F. I. Sonntag, *J. Am. Chem. Soc.*, **86**, 3179 (1964).

[3] D. M. Hercules, *Science*, **145**, 808 (1964).

[4] (a) R. E. Visco and E. A. Chandross, *J. Am. Chem. Soc.*, **86**, 5350 (1964); (b) K. S. V. Santhanam and A. J. Bard, *ibid.*, **87**, 139 (1965).

[5] E. A. Chandross, J. W. Longworth, and R. E. Visco, *ibid.*, **87**, 3259 (1965).

have shown evidence for a mechanism involving the formation of excimers. Instead of reactions 4, 5, and 6, the following reactions could occur.

$$R^+ + R^- \xrightarrow{k_4'} R_2^* \qquad (4')$$

$$R_2^* \xrightarrow{k_5'} 2R + h\nu' \qquad (5')$$

$$R_2^* \xrightarrow{k_6'} 2R \qquad (6')$$

In the ensuing discussion these two mechanisms are effectively identical.

The purpose of this paper is to relate quantitatively the light intensity produced in electrogenerated chemiluminescence to the current, time, and kinetic parameters. These relationships have been calculated for a double potential step mode of generation as used by Santhanam and Bard.[4b] The general details of this electrochemical technique were first described by Schwartz and Shain.[6] The electrode potential is initially set so that zero current flows. A sufficiently positive potential pulse of duration t_f is applied so that the concentration of species R at the electrode surface instantaneously becomes zero as reaction 1 proceeds. The positive pulse is immediately followed by a negative potential pulse of duration t_r so that the surface concentrations of both species R and R^+ are zero as reactions 2 and 3 proceed. During the negative pulse, reactions 4 and 5 proceed in the diffusion layer producing light, the intensity of which can be measured using a photomultiplier tube coupled with an oscilloscope.[4b] It is possible, of course, to generate the anion radical first. This case is exactly analogous to that described by reactions 1–7.

The moles of photons generated per unit time will depend on several factors: (a) C_R, the bulk concentration of species R; (b) D, the diffusion coefficient of species R, R^-, R^+, etc.; (c) A, the electrode area; (d) t_r and t_f, the duration of the potential pulses; (e) k_4, the bimolecular rate constant for reaction 4; and (f) φ, the fraction of excited species R* or R_2^* undergoing radiative decay

$$\varphi = k_5/(k_5 + k_6 + k_7[R]_{x,t})$$

The theoretical analysis of this problem was accomplished using a computer approach previously described in detail by Feldberg and Auerbach[7] in the analysis of second-order kinetic effects in chronopotentiometry, and more recently by Feldberg[8] in the analysis of kinetic effects at the dropping mercury electrode. The method is particularly applicable to solving problems which lead to nonlinear partial differential equations. The basis of the method is a simple model: the solution is considered as an array of small homogeneous volume elements parallel to the electrode surface. Diffusion is simply the transfer of material from one volume element to another, while kinetic calculations for reactions within each homogeneous volume element become quite straightforward. The computer program is written in Fortran language for the IBM 7094 digital computer. The boundary conditions are: $t = 0$, $[R] = C_R$ from $x = 0$ to $x = \infty$; $0 < t \leq t_f$, $[R]_{x=0} = 0$; $t_f < t \leq (t_r + t_f)$, $[R]_{x=0} = 0$, and $[R^+]_{x=0} = 0$.

Three assumptions are made: (i) radiative decay is very fast (rate constants for fluorescence are well known to be of the order of 10^8 sec^{-1}); (ii) mass transport is diffusion controlled and $D = D_R = D_{R^+} = D_{R^-} \ldots$ etc.; (iii) $k_7 = 0$.[9]

The results of the computer calculations are presented in terms of the following normalized dimensionless quantities, ω, θ, β, and ψ where

$$\omega = \frac{I t_f^{1/2}}{\varphi A C_R D^{1/2}} \qquad (8a)$$

or since

$$i_f = \frac{F A C_R D^{1/2}}{(\pi t_f)^{1/2}} \qquad (8b)$$

$$\omega = \frac{IF}{\pi^{1/2} \varphi i_f} \qquad (8c)$$

$$\theta = t_r/t_f \qquad (9)$$

$$\beta = i_r/i_f \qquad (10)$$

and

$$\psi = k_4 t_f C_R \qquad (11)$$

where I is the rate of light emission in moles of photons/sec; F is the Faraday; i_r and i_f are the currents at t_r and t_f, respectively; and k_4 is the bimolecular rate constant for reaction 4.

Current–Time Relationship. Although the current–time relationship is obtained directly from the computer calculations (Figure 1, curve 2), the relationship may be easily derived. Simple reasoning can show that both i_f and i_r are independent of the kinetics of reaction 4. That i_f is independent of k_4 is obvious since it depends only upon the diffusion of species R to the electrode surface (eq. 8b). Independence of i_r may be shown by considering an infinitesimally small volume element containing a_{R^+}, b_{R^-}, and c_R (assuming $k_4 = 0$) generated during the first potential pulse. During the second potential pulse $2a + c$ electrons will be required to reduce everything to R^-. If $k_4 = \infty$, and $a > b$, the volume element would contain $(a - b)_{R^+}$ and $(2b + c)_R$, and $2(a - b) + 2b + c$ or $2a + c$ electrons are still required to reduce everything to R^-. Similarly for any value of k between 0 and ∞, $2a + c$ electrons are required. The reasoning is analogous for the case where $b > a$.

The mathematical relationship between i_r/i_f and t_r/t_f is easily derived by first considering the simple case involving only one couple where

$$R \longrightarrow R^+ + e^- \qquad \text{first potential pulse} \qquad (12)$$

$$e^- + R^+ \longrightarrow R \qquad \text{second potential pulse} \qquad (13)$$

Hawley[10] has derived the following from the equations of Smit and Wijnen.[11]

$$\frac{i_r}{i_f} = \frac{(1 + \theta)^{1/2} - \theta^{1/2}}{\theta^{1/2}(1 + \theta)^{1/2}} \qquad (14)$$

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(6) W. M. Schwartz and I. Shain, *J. Phys. Chem.*, **69**, 30 (1965).

(7) S. W. Feldberg and C. Auerbach, *Anal. Chem.*, **36**, 505 (1964).

(8) S. W. Feldberg, presented at the meeting of the Electrochemical Society, San Francisco, Calif., May 1965, Abstract No. 156.

(9) Initial calculations are made assuming $k_7 = 0$ for the self-quenching reaction 7. It will be shown that the effect of self-quenching is easily evaluated on the basis of these initial calculations.

(10) D. M. Hawley, Dow Chemical Corp., Midland, Mich., private communication.

(11) W. M. Smit and M. D. Wijnen, *Rec. Trav. Chim.*, **79**, 5 (1960).

$$i_r = i_f\frac{(1+\theta)^{1/2} - \theta^{1/2}}{\theta^{1/2}(1+\theta)^{1/2}} \qquad (15)$$

Equation 14 has been verified using the computer technique and is plotted in Figure 1, curve 1. For the mechanism in which we are interested one must consider reaction 13 plus the reduction of species R to R^- (reaction 2). Once reaction 13 has occurred, we have at the electrode surface the bulk concentration of R, C_R. Thus there is an additional current component to be added to eq 15

$$i_r' = \frac{FAC_RD^{1/2}}{(\pi t_r)^{1/2}} \qquad (16)$$

Thus

$$i_r = i_f\frac{(1+\theta)^{1/2} - \theta^{1/2}}{\theta^{1/2}(1+\theta)^{1/2}} + \frac{FAC_RD^{1/2}}{(\pi t_r)^{1/2}} \qquad (17)$$

Substituting from eq 8b and rearranging gives

$$\frac{i_r}{i_f} = \frac{(1+\theta)^{1/2} - \theta^{1/2}}{\theta^{1/2}(1+\theta)^{1/2}} + \frac{1}{\theta^{1/2}} = \frac{2(1+\theta)^{1/2} - \theta^{1/2}}{\theta^{1/2}(1+\theta)^{1/2}} \qquad (18)$$

Equation 18 agrees exactly with the computer calculations (curve 2, Figure 1).

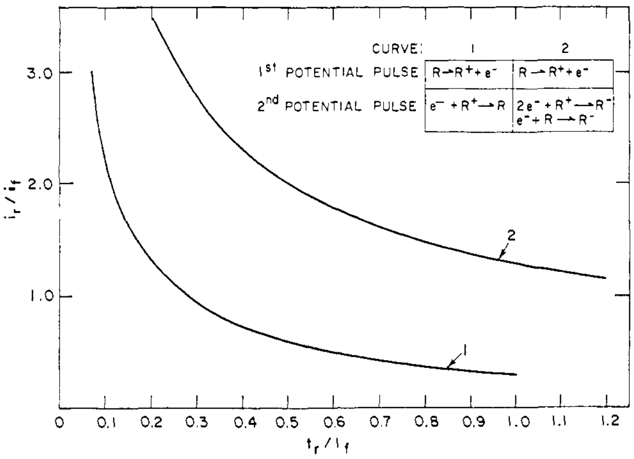

Figure 1. Normalized current–time relationship.

By comparing current–time data with curve 2, Figure 1, one can verify only the over-all stoichiometry of the reactions. Deviations from theory may have several explanations: formation of R^{-2}, or R^{+2}, possibly resulting from the improper choice of the size of the potential pulses; side reactions of the generated radicals; or impurities.

Light Intensity–Time Relationship. The normalized plot, log ω *vs.* $(t_r/t_f)^{1/2}$ is shown in Figure 2. As the parameter $k_4t_fC_R$ increases to larger values, the plot achieves a maximum negative slope of -1.45 when $k_4t_fC_R \geq 10^3$ indicating the shift from kinetically controlled to diffusion-controlled light emission.

Interpretation of the experimental data is quite straightforward. The output, P, of a photomultiplier tube is followed as a function of time. Defining

$$f = I/P_x \qquad (19)$$

it is clear from the definition of ω (eq 8a and 8c) that a plot of log P *vs.* $(t_r/t_f)^{1/2}$ will have the same form as one of the curves in Figure 2, depending upon the value of

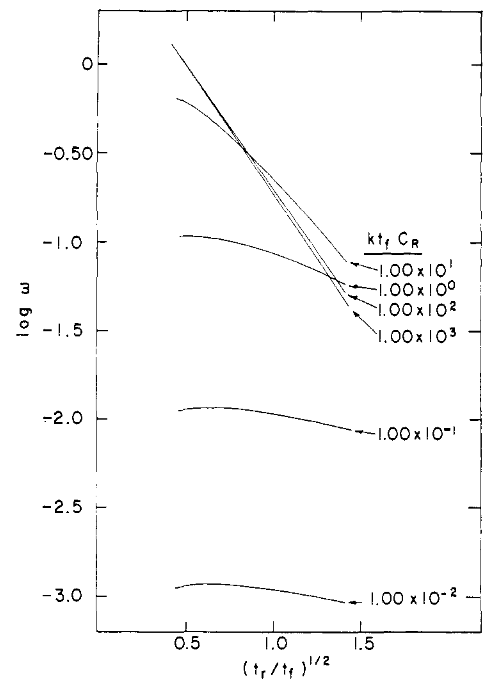

Figure 2. Normalized light intensity–time relationship.

$k_4t_fC_R$. Preliminary studies of rubrene in dimethylformamide[12] indicate that k_4 is very large and that the chemiluminescence is diffusion controlled; *i.e.*, $k_4t_fC_R > 10^3$. From Figure 2 one can write the following expression for diffusion-controlled chemiluminescence.

$$\log \omega = -1.45(t_r/t_f)^{1/2} + 0.71 \qquad (20)$$

Combining eq 8c, 19, and 20 gives

$$\log \frac{fPF}{\pi^{1/2}\varphi i_f} = -1.45(t_r/t_f)^{1/2} + 0.71 \qquad (21)$$

If the output of the photomultiplier can be calibrated, *i.e.*, the value of f (eq 19) determined, the quantum efficiency φ can be determined. Here again, conformance with theoretical behavior can only verify the generalized mechanism.

Effect of Self-Quenching. Using the computer one can calculate the concentration and light emission profiles for the electrogeneration of chemiluminescence. A sample set of profiles is shown in Figure 3 for the three species R^+, R^-, and R (curves 1 to 6) and for the light emission (curves 7 and 8). The odd-numbered solid curves correspond to $k_4t_fC_R = 1.00 \times 10^3$ while the even-numbered dashed curves correspond to $k_4t_fC_R = \infty$. Light emission is distributed over the diffusion layer. As the value of the bimolecular rate constant k_4 approaches infinity, all light emission occurs in an infinitely thin plane parallel to the electrode surface. (This assumes that k_5 is infinitely fast which of course is not true.) From Figure 3 it can be seen that the concentration of species R in the plane of light emission approaches C_R as $k_4 \rightarrow \infty$. Thus, the quantum efficiency φ, which has been defined as

$$\varphi = \frac{k_5}{k_5 + k_6 + k_7[R]_{x,t}} \qquad (22)$$

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[12] R. C. Lansbury, D. M. Hercules, and D. K. Roe, Massachusetts Institute of Technology, Cambridge, Mass., private communication.

may be redefined

$$\varphi = \frac{k_5}{k_5 + k_6 + k_7 C_R} \tag{23}$$

It is clear that quantum efficiency is a function of concentration and that the effect of varying C_R upon the value of φ will depend upon the relative magnitudes of k_5, k_6, and $k_7 C_R$.

Unless the photomultiplier is calibrated, φ is indeterminate, but one can determine φ/f from eq 21. Defining a new constant

$$\varphi' = \varphi/f \tag{24}$$

multiplying eq. 23 by the term $1/f$, substituting from eq 24, and rearranging, gives

$$\frac{1}{\varphi'} = f + \frac{fk_6}{k_5} + \frac{fk_7 C_R}{k_5} \tag{25}$$

From eq. 25 one can see that a plot of $1/\varphi'$ *vs.* C_R should be a straight line having a slope of fk_7/k_5 and an intercept of $f(1 + k_6/k_5)$. If self-quenching is negligible, the line will have zero slope. It must be pointed out that impurities associated with the organic species R may have a quenching effect which would manifest itself as self-quenching.

Other Quenching Effects. The excited molecule R* can also be quenched by reactions of the type

$$Z + R^* \xrightarrow{k_{26}} R + Z^* \tag{26}$$

where species Z is the solvent, supporting electrolyte, or an impurity. If the reaction is pseudo first order,[13] one can write eq 25 in a completely general form

$$\frac{1}{\varphi'} = f + \frac{fk_6}{k_5} + \frac{fk_7 C_R}{k_5} + f \sum_{i=10}^{n} \frac{C_i k_i}{k_5} \tag{27}$$

where k_i is the rate constant for the reaction of R* with the ith species of concentration C_i. Experimentally the concentration of certain of these species can be varied, *e.g.*, supporting electrolyte, and the effect noted by plotting $1/\varphi'$ *vs.* C_i. One could not determine if an observed effect was actually due to quenching by the supporting electrolyte or due to impurities associated with the supporting electrolyte.

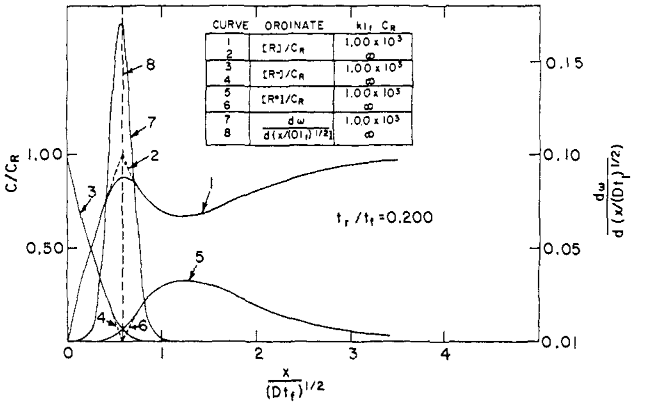

Figure 3. Normalized concentration profile and light emission profile.

Acknowledgments. The author thanks Professor D. K. Roe, Massachusetts Institute of Technology, Cambridge, Mass. (who suggested that these calculations be made); Dr. R. E. Visco, Bell Telephone Laboratories, Inc., Murray Hill, N. J.; and Dr. Jack Fajer and Dr. Norman Sutin, Brookhaven National Laboratory, Upton, N. Y., for interesting and helpful discussions and suggestions.

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(13) For reaction 10 to be pseudo first order, the concentration of Z must be much greater than that of R*, or decay of Z* to Z must be much faster than the rate of consumption of Z.