

electron transfer in the weller group at the free university in amsterdam (1964-1971)

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Prelude: Fluorescence Quenching and Electron Transfer Before 1961

The understanding of electron transfer in the excited state originated during the discussions of the mechanism underlying fluorescence quenching. At the time,^{1,2} it was considered to be surprising that molecules in the singlet excited state could survive the collisions with the surrounding molecules at all and it was thought that only those molecular systems would fluoresce in which the excited state is screened against reactive collisions.¹ Such inelastic collisions were believed to involve a chemical reaction or a molecular dissociation process, as it was realized that the probability of degrading electronic excitation energy into a large number of vibrational quanta would be very small.

Electron transfer was discussed in relation with the inner mechanism of fluorescence quenching. In 1932 Baur suggested that this quenching occurs via “molecular electrolysis by the redox agent”.² He thereby stressed that his theory found the solution for a problem that could not be solved by the “usual requisites of molecular theoreticians, i.e., collisions”. Franck and Levi (1935) mentioned a number of cases in which an electron is “snatched” from a fluorescing molecule by the quencher: a redox reaction. An example was the photooxidation of aniline by chlorophyll in the excited state.¹ Weiss and Fischgold (1936) then considered the reaction to be a simple electron transfer process from the quencher (such as the inorganic ions Fe^{2+} or Cl^-) to the excited molecule.³ They also noted that the electron affinity of a molecule increases upon excitation. The electron transfer assumption appeared to be reasonable, as it was correctly understood that only such a reaction (no chemical bonds broken) would be fast enough to compete with the short-lived (nanoseconds) fluorescence.⁴ The early history of fluorescence quenching is discussed in the book of Theodor Förster.⁴

Electron Transfer in the Excited Singlet State Leonhardt and Weller 1961

The first direct experimental proof that the inner mechanism of fluorescence quenching involves electron transfer was published by Leonhardt and Weller in 1961.⁵ By using flash photolysis, the presence of the radical anion of perylene (Pe^-) was detected in the excited-state transient absorption spectrum of a solution of the electron acceptor(A)/donor(D) system perylene/*N,N*-dimethylaniline (DMA) in acetonitrile (eq 1).



The perylene anion brought Weller into contact with Jan Hoijtink, then Professor of Physical Chemistry at the Free University (VU) in Amsterdam, who had published the absorption spectrum of Pe^- as part of his experimental and theoretical studies on radical anions of aromatic hydrocarbons. After Hoijtink accepted a position at the Municipal University of Amsterdam in 1960, Weller became his successor at the VU in 1962.

Exciplexes

When Weller moved from Stuttgart to Amsterdam, his main interest still was proton transfer. This can be seen from his Inaugural Oration “Het Proton in de Fysische Chemie” (1963). But attention rapidly switched to electron transfer. The first example (found in Stuttgart) of a fluorescing intermediate in the quenching reaction between ${}^1\text{A}^*$ and D, an “excited charge-transfer complex” ${}^1(\text{A}\cdot\text{D}^+)$,⁶ was reported in 1963 for perylene/DMA in a nonpolar or weakly polar solvent.⁷

Exciplex formation was investigated by fluorescence measurements in a variety of solvents as a function of polarity and temperature.^{8,13} In addition, the phosphorescence and E-type delayed fluorescence of triplet exciplexes ${}^3(\text{A}\cdot\text{D}^+)$ were studied in low-temperature glasses.^{11,14} Amino-substituted benzenes such as DMA, *N,N*-diethylaniline (DEA) and *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) were employed as the donor, with aromatic hydrocarbons such as perylene, anthracene or biphenyl as acceptor. Either ${}^1\text{A}^*$ or ${}^1\text{D}^*$ was the primarily excited species (eqs 2 and 3), see Figure 1: (a) ${}^1\text{anthracene}^* + \text{DEA}$ and (b) biphenyl + ${}^1\text{DEA}^*$. Aromatic hydrocarbons can also act as donor, in a reaction with a strong acceptor such as 1,4-dicyanobenzene.⁸



The requirement for exciplex formation clearly is that the energy $E({}^1(\text{A}\cdot\text{D}^+))$ is smaller than that of ${}^1\text{A}^*$ or ${}^1\text{D}^*$. The same requirement also appeared to hold for triplet exciplexes ${}^3(\text{A}\cdot\text{D}^+)$ with respect to both monomer triplet states ${}^3\text{A}^*$ and ${}^3\text{D}^*$. This condition means that exciplex phosphorescence generally can only be detected with A/D systems having relatively high triplet energies such as benzene derivatives (benzonitrile, dicyanobenzenes) as acceptor and anilines as donor, but not for molecules with low-energy triplet states such as anthracene. The triplet exciplexes ${}^3(\text{A}\cdot\text{D}^+)$ with D = DEA and A = benzonitrile and *s*-triazine were also

investigated by ESR.^{13,14} Later, a large number of triplet exciplexes were studied at the MPI in Göttingen, by measuring their phosphorescence and ESR spectra.^{15,16}

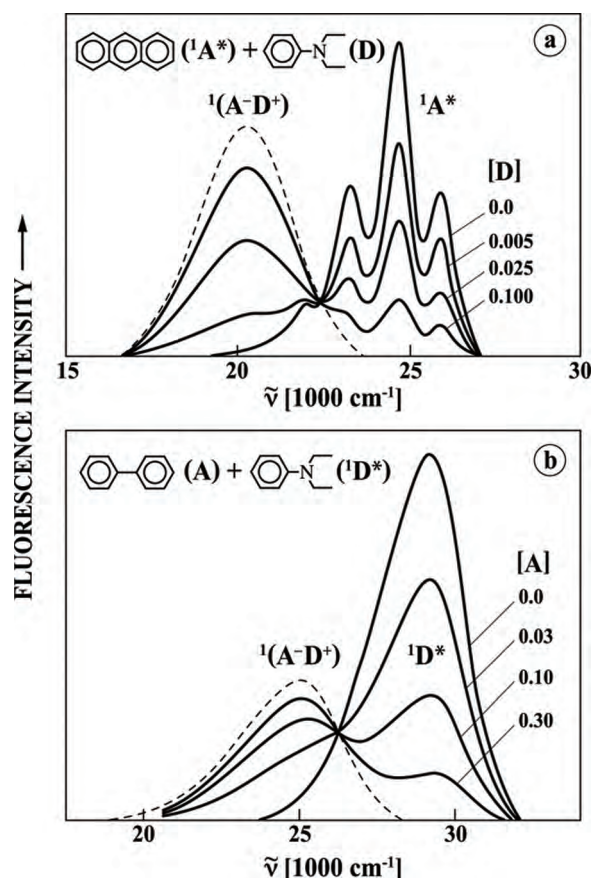


Figure 1. Fluorescence spectra in toluene at room temperature consisting of two emissions, from an exciplex ${}^1(A\cdot D^+)$ and from a monomer ${}^1A^*$ or ${}^1D^*$ in the excited singlet state. (a) Anthracene (${}^1A^*$) with *N,N*-diethylaniline (DEA) and (b) DEA (${}^1D^*$) with biphenyl. The dashed lines represent the exciplex spectra extrapolated to infinite quencher concentration.

The Weller Equation

In order to estimate the energetic feasibility to produce exciplexes via the reactions ${}^1A^* + D$ or $A + {}^1D^*$ (eqs 2 and 3), the exciplex energy $E(A\cdot D^+)$ should be known. This energy was determined by measuring as a function of temperature the exciplex-to-monomer fluorescence intensity ratio I/I_c of A/D systems in a nonpolar solvent (Figure 2).^{10,12} From these data, the exciplex stabilization enthalpy ΔH is determined, which gives $E(A\cdot D^+) = E({}^1A^*) + \Delta H$.

DEA or triethylamine (TEA) was the donor, whereas anthracene, 1,2-benzanthracene, biphenyl, naphthalene,

perylene and pyrene were acceptors. These measurements reveal that the energy of an exciplex ${}^1(A\cdot D^+)$ with full electron transfer in *n*-hexane at room temperature is equal to the difference between the redox potentials $E_{\text{ox}}(D/D^+)$ and $E_{\text{red}}(A^+/A)$ (in acetonitrile or dimethylformamide) and a semiempirical term 0.15 eV: the Weller equation (eq 4).^{10,12}

$$E(A\cdot D^+)^{\text{hex}} = E_{\text{ox}}(D/D^+) - E_{\text{red}}(A^+/A) + 0.15 \pm 0.10 \text{ eV} \quad (4)$$

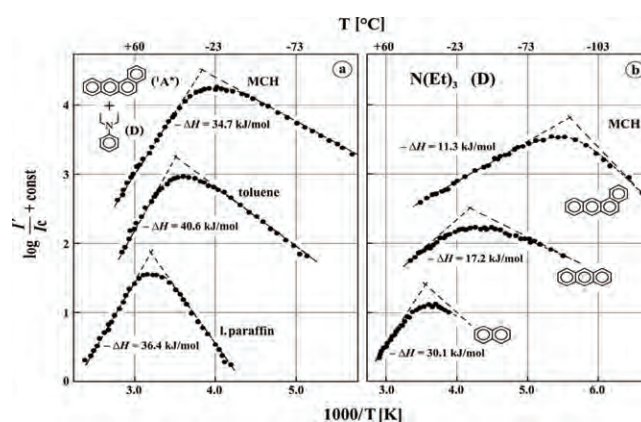


Figure 2. Plots of $\log(I/I_c)$ against the reciprocal absolute temperature, where I/I_c is the exciplex-to-monomer fluorescence intensity ratio (at the emission maxima) and c is the quencher concentration $[D]$, for the ${}^1A^*/D$ systems (a) 1,2-benzanthracene and *N,N*-diethylaniline (DEA) in methylcyclohexane (MCH), toluene and liquid paraffin and (b) triethylamine (NEt_3) as D and 1,2-benzanthracene, anthracene and naphthalene as A . The exciplex stabilization enthalpy $-\Delta H$ is indicated at the high-temperature part of the plots.

Approximations in the Weller Equation

Equation 4 generally only gives an approximate value (± 0.10 eV) for $E(A\cdot D^+)$. The reasons are the following: a) the entropy change ΔS of exciplex formation is assumed to be constant. In fact, a linear $\Delta H/\Delta S$ correlation will exist,¹⁷ so that eq 4 underestimates the possibility of exciplex formation for A/D couples with small $-\Delta H$. b) the Coulomb energy $C(A\cdot D^+)$ is also assumed to be constant. In reality, this energy depends on the degree of charge delocalization in A^+ and D^+ . The energy of an exciplex with DMA or DEA as the donor (for which anilines the semiempirical term 0.15 eV in eq 4 was derived) will therefore be larger (smaller $C(A\cdot D^+)$) than that for an exciplex of the same acceptor with TEA, having a radical cation with the positive charge largely concentrated on the amino nitrogen. When the Weller equation is used in a comparison of exciplex data for DEA and TEA, the oxidation potential of TEA should hence be corrected for this $C(A\cdot D^+)$ effect.

Classification of Molecular Complexes

A theoretical treatment of molecular complexes between aromatic electron donors and acceptors was developed by Henk Beens (Figure 3).^{13,18} A classification of complexes (AD)* was based on the percentage of the various zero order states (A·D⁺), (A⁺D[·]), (A*·D), (AD*) and (A-D) in their VB-wavefunction (eq 5).¹⁹

$$\Psi_{\text{exc}}(\text{AD})^* = e_1\psi(\text{A}\cdot\text{D}^+) + e_2\psi(\text{A}^+\text{D}\cdot) + e_3\psi(\text{A}^*\text{D}) + e_4\psi(\text{AD}^*) + e_5\psi(\text{A-D}) \quad (5)$$

Four different kinds of molecular complexes are defined: (a) *exciplexes* (A·D⁺): effectively “full” CT: $e_1 = 1$. (b) *mixed excimers*: significant contribution of (A*·D) and/or (AD*). (c) *EDA complexes* in the ground state S₀: main contribution of (A-D) with some (A·D⁺). (d) *excimers* constitute a special case of eq 5, with A = D and equal contributions of (A·A⁺) and (A⁺A[·]) as well as of A*·A and AA*.



Figure 3. Klaas Zachariasse (left) and Henk Beens (right) in the cellar of the Scheikundig Laboratorium of the VU surrounded by chemicals, dewars and papers, during a (rare) period that the fluorescence “machine” was out of order.

Courtesy of Klaas Zachariasse

Triple Exciplex

During the investigation of the fluorescence quenching of 1,4-dicyanobenzene (A) by naphthalene (D), it was observed that by increasing the naphthalene concentration a new additional emission band started to appear to the red of the (A·D⁺) exciplex fluorescence. This new band was attributed to a triple exciplex AAD. That its structure was AAD, and not ADA, was established by way of a dipole moment measurement.²⁰

Bianthryl and Excimers (AA)*

The Role of Symmetry Breaking

The VB-treatment was also applied to excimers (AA)* and symmetric molecules such as 9,9'-bianthryl with two

identical aromatic moieties. When the energy of the zero order CT state (A·A⁺) is lower than that of (A*·A) (eq 4), formation of an S₁ state with a nonzero overall dipole moment, that is, a CT state, will become possible.²¹ The breaking of symmetry does not play a negative or positive role on a molecular scale in such biaryls or excimers, as statistically an equal amount of (A·A⁺) and (A⁺A[·]) states will be formed. As soon as the electron is transferred to create either (A·A⁺) or (A⁺A[·]), the solvent will stabilize this CT state and its existence is solely based on energetic grounds.

Radical Ion Chemiluminescence

As radical ions A[·] and D⁺ are formed in the fluorescence quenching of perylene (¹A*) by DMA (D) in acetonitrile (eq 1),⁵ the question arose whether the reverse process would be possible (eq 6).



Examples of the generation of molecules in the singlet excited state (S₁) from radical ions were already known:^{22,23} the electrochemiluminescence from aromatic hydrocarbon ions by Hercules and Chandross (later called the S route).²⁴

The first attempt to observe chemiluminescence from radical ions A[·] and D⁺ (eq 6) was made in October 1964. The main initial problem clearly was how to prepare A[·] and D⁺. As radical cation, the well-known stable TMPD⁺ClO₄⁻ (Wurster's Blue perchlorate) was chosen. The technique to make radical anions of aromatic hydrocarbons with alkali metal films in evacuated pyrex cells was well-established at the VU, inherited from Hoijtink (Figure 4). With the advise



Figure 4. The author preparing an evacuated pyrex chemiluminescence cell. Safety considerations did not get top priority at the time: a laboratory coat or safety glasses, although available (see photograph), were not always used.

Courtesy of Klaas Zachariasse

of Nel Velthorst, a solution of perylene radical anion in 1,2-dimethoxyethane (DME) was prepared. Upon pouring this solution on solid $\text{TMPD}^+\text{ClO}_4^-$, a bright violet chemiluminescence emerged, the fluorescence of perylene.

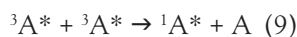
From the free enthalpy $\Delta G(\text{A}^-\dots\text{D}^+)$ stored chemically in the solvent-separated ion-pair in DME (eq 7),^{25,26} the chemical excitation energy, it became clear that the chemiluminescence from the S_1 state of perylene could only have originated from triplet-triplet annihilation (TTA) of two molecules in the triplet state (eqs 8 and 9), the first example of chemiluminescence via the T-route (Figure 5).^{25,27-30}

$$\Delta G(\text{A}^-\dots\text{D}^+)^{\text{DME}} = E_{\text{ox}}(\text{D}/\text{D}^+) - E_{\text{red}}(\text{A}^-/\text{A}) + 0.20 \text{ eV} \quad (7)$$



Figure 5. Blue anthracene fluorescence as chemiluminescence from a reaction between anthracene- Na^+ and $\text{TMPD}^+\text{ClO}_4^-$ in 1,2-dimethoxyethane. The fluorescence originates by triplet-triplet annihilation from the initially produced anthracene triplets. Insert: the evacuated pyrex chemiluminescence cell.

followed by TTA:



An experimental confirmation of this conclusion was that no chemiluminescence results from the reaction between the radical anion of pentacene and $\text{TMPD}^+\text{ClO}_4^-$: the energy of two pentacene triplets being smaller than the energy $E(\text{S}_1)$.^{25,27-29} In the A^-/TMPD^+ reaction with the anions of pyrene and 9,10-dimethylantracene, the chemiluminescence spectrum consists of monomer and excimer emissions, both produced by TTA (E-route).^{25,27-29}

Larger Intermolecular Distance for Charge Recombination than for Charge Separation

With bitolyl/ TMPD^+ (Figure 6a), ${}^3\text{A}^*$ as well as ${}^3\text{D}^*$ is energetically accessible and hence produced in the radical ion recombination (eqs 8 and 10).^{25,28,31,32} The ${}^1\text{A}^*$ and ${}^1\text{D}^*$ fluorescence in the chemiluminescence spectrum is brought about by homogeneous TTA (eqs 9 and 11). Exciplex formation occurs by mixed TTA (eq 12), as well as directly from the radical ions (eq 13).^{25,28,30-32}

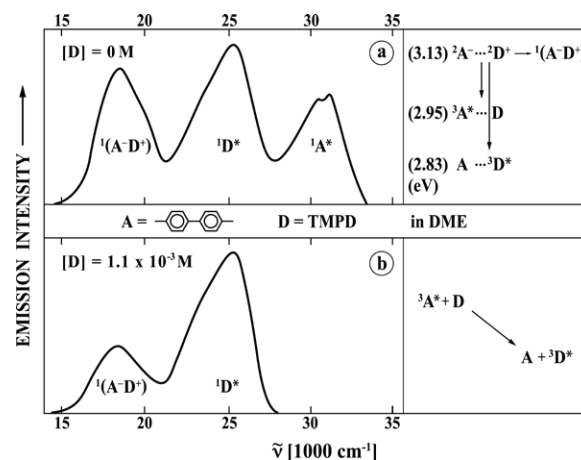
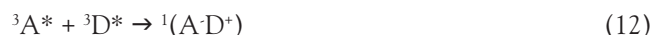


Figure 6. (a) Chemiluminescence spectrum from a reaction between bitolyl (A^-) and TMPD^+ (D^+) in 1,2-dimethoxyethane (DME) at room temperature, with emissions from ${}^1\text{A}^*$, ${}^1\text{D}^*$ and ${}^1(\text{A}^-\text{D}^+)$. (b) Chemiluminescence spectrum from bitolyl/ TMPD^+ with added TMPD ($1.1 \times 10^{-3} \text{ M}$). The bitolyl (${}^1\text{A}^*$) fluorescence is absent, as ${}^3\text{A}^*$ is quenched by TMPD (eq 14), see scheme to the right.

When triplet formation would take place in a collision complex of A^- and D^+ , it should be expected that only the molecule having the lowest triplet energy (here ${}^3\text{TMPD}^*$, Figure 6a) remains excited, as ${}^3\text{A}^*\text{D}$ would undergo triplet-triplet energy transfer, giving A^3D^* . The experimental observation (Figure 6a) that both triplets ${}^3\text{A}^*$ and ${}^3\text{D}^*$ are generated in the A^-/D^+ reaction, shows that triplet formation occurs at an intermolecular separation of A^- and D^+ larger than the collision distance at which the triplet energy transfer (eq 14) takes place. This conclusion is supported by chemiluminescence experiments of bitolyl/ TMPD^+ with added TMPD , showing the disappearance of the bitolyl fluorescence caused by triplet energy transfer from ${}^3\text{A}^*$ to ${}^3\text{D}^*$ (Figure 6b).^{25,31,32}

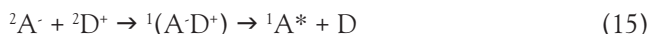


These results make clear that in an A/D system the charge recombination between A^- and D^+ occurs at a larger

intermolecular distance than the charge separation between ${}^1A^*$ and D, which reaction is supposed to operate at the same collisional A/D distance as the triplet-triplet energy transfer (eq 14). This difference in reaction pathway constitutes a violation of the principle of microscopic reversibility (see below).

Direct Exciplex Formation from the Radical Ions A^- and D^+

The direct generation of ${}^1(A\cdot D^+)$ from the radical ions (eq 13) is an efficient process in A^-/D^+ reactions of *p*-substituted triphenylamines with methyl, methoxy and dimethylamino substituents as the radical cation.^{25,30-33} An example is the chemiluminescent reaction between the cation of tri-*p*-tolylamine (TPTA⁺) and the radical anions of anthracene, 9-methylanthracene and 9,10-dimethylanthracene.^{25,33} The production of ${}^1A^*$ takes place via a thermal reaction from the initially prepared exciplex (eq 15), having an energy close to that of ${}^1A^*$.³³ For these TPTA⁺/ A^- reactions, a magnetic field effect (1400 gauss) is not detected, in contrast to bitolyl/TMPD⁺ and related systems for which only mixed and homogeneous TTA leads to chemiluminescence.^{25,32}



Chemiluminescence spectra only consisting of an ${}^1(A\cdot D^+)$ emission (eq 13) were obtained when the chemical excitation energy $\Delta G(A^- \dots D^+)$ is below that of both monomer triplets ${}^3A^*$ and ${}^3D^*$, making thermal formation of the excited singlet states (eq 15) impossible. Examples are $A^-/TPTA^+$ systems with 1,4-dicyanobenzene, trans-stilbene or benzophenone as the acceptor A and trans-stilbene/TPDA⁺ (TPDA = tris(*p*-dimethylaminophenyl)amine).^{25,31,32} The mechanisms developed for radical ion recombination reactions of the chemically prepared ions A^- and D^+ (eqs 6, 8-13, 15), phenomena operating in OLEDs, are identical to those leading to electrochemiluminescence, the only difference being that there the radical ions are prepared at electrodes.^{24,25}

Chemiluminescence Quantum Yields

Direct formation of ${}^1A^*$ via the exciplex (eq 15) results in relatively large chemiluminescence quantum yields. For TPTA⁺/9,10-dimethylanthracene⁻ in tetrahydrofuran, a quantum yield of 7.5% was obtained by a direct light measurement with the kaliumferrioxalate actinometer.³⁰ For systems TMPD⁺/ A^- , in which ${}^1A^*$ is produced indirectly via TTA, considerably smaller yields of the order of 10^{-4} to 10^{-5} were determined.³⁰

Chemiluminescence with Solvated Electrons

Generation of molecules in the excited singlet state without the presence of radical anions A^- was achieved with TMPD⁺ClO₄⁻ and a solution of a K/Na alloy in DME.²⁵ This involves the direct formation of ${}^1D^*$ from TMPD⁺ and solvated electrons (eq 16).



Chemiluminescence and Marcus Theory Microscopic Reversibility

During the investigation of the radical ion recombination chemiluminescence,²⁵ the role of Marcus theory³⁴ in charge separation and recombination was strongly debated in the Weller group. Although the present author was convinced that the inverted chemical effect of Marcus theory was the mechanism governing the chemiluminescence, see Figures 7 and 8,²⁵ Weller did not share this opinion. His skepticism

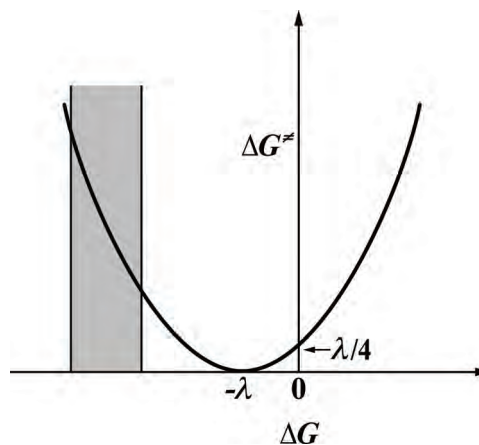


Figure 7. Dependence of the free activation enthalpy ΔG^\ddagger on the reaction free enthalpy ΔG for (chemiluminescent) electron transfer reactions $A^- \dots D^+ \rightarrow (AD)^*$. The reorganization energy λ from the Marcus theory (eq 17, ref 34) is indicated in the figure. Its value for the recombination chemiluminescence is determined from experimental data on the isotopic exchange reactions $A^- + A$ and $D + D^+$ with $\Delta G = 0$ (ref 25). Chemiluminescent reactions described here (refs 25, 27-33) have a ΔG in the shaded area and are clearly in the region of the inverted chemical effect.

was based on the principle of microscopic reversibility, that is, the idea that a reaction $A \rightarrow B$ will follow the same pathway as the reverse process $B \rightarrow A$. Because the fluorescence quenching rate constant (eq 1) in acetonitrile does not decrease for large $-\Delta G$, the Rehm-Weller plot,³⁵ it was assumed that an inverted chemical effect was also not to be expected for the recombination reaction (eq 6).

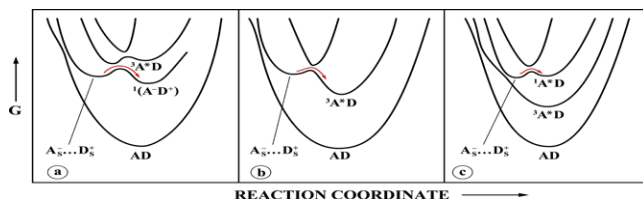


Figure 8. Potential energy curves, based on the Marcus theory of electron transfer (ref 34), for reactions starting from the solvent separated ion pair ($A^{\cdot-} \dots D^{\cdot+}$), with (a) $\Delta G(A^{\cdot-} \dots D^{\cdot+}) < E(^3A^*)$, (b) $\Delta G(A^{\cdot-} \dots D^{\cdot+}) > E(^3A^*)$ and (c) $\Delta G(A^{\cdot-} \dots D^{\cdot+}) \approx E(^1A^*)$. In (b), the exciplex $^1(A^*D)$ can be formed from ($A^{\cdot-} \dots D^{\cdot+}$). The reaction to the ground state AD is suppressed by the inverted chemical effect. The figure is adapted from ref 25.

In the late sixties, Marcus theory was not widely discussed in publications on electron transfer. When the author presented this subject at Daudel's Summer Course on Quantum Chemistry in Menton in July 1968, the inverted chemical effect met with disbelief, although it was shown that the Marcus equation eq 17 with the dependence of ΔG^{\ddagger} on ΔG and the reorganization energy λ was, at least algebraically (two intersecting parabolae, harmonic approximation) similar to the equations for electrochemical electron transfer and the strong coupling limit of radiationless transitions.^{34,36,37}

$$\Delta G^{\ddagger} = \frac{\lambda}{4} \left(1 + \frac{\Delta G}{\lambda} \right)^2 \quad (17)$$

The uncertainty in the width and relative location of the parabolae used in the illustration of the inverted chemical effect (Figure 8) were seen as an argument against the general applicability and predictive power of the theory. This attitude prevailed in the seventies. The appreciation of Marcus Theory made a full turn after the charge-shift experiments of Miller and Closs.³⁸ The discrepancy noted by Weller is, however, still unresolved. This discrepancy that the inverted chemical effect controls charge recombination reactions, but plays a much smaller role in charge separation reactions, may be due to a difference in reaction path, in particular the difference in electron transfer distance as discussed above (Figure 6).

Instruments Used in the Experiments

The equipment available for the Weller group at the Chemistry Laboratory of the VU in Amsterdam was rather simple, as at the time probably practically everywhere. The perhaps most important piece of equipment was a fluorescence machine, designed in Stuttgart. Its central element

was a rotating prism, making a peculiar sound which led to the nickname "vogel" (bird). This construction principle enabled the recording of a complete emission spectrum in a few seconds. The spectrum appeared on the screen of an oscilloscope and had hence to be photographed. The developing and drying of the films and the drawing by pencil of the enlarged spectra on graph paper took up a considerable part of the time needed to carry out an experiment. Nevertheless, the fact that the spectra could be measured so fast with the fluorescing sample in full view in the darkened room, made rapid testing easily possible, a great advantage during the early exploratory stage of research in which the conditions necessary for exciplex formation were investigated. The rapid scanning and recording of the spectra were particularly important for the chemiluminescence studies employing a flow-cell in which a solution of a radical anion flowed through a solid radical cation salt such as the perchlorates of Wurster's Blue or cations of tri-*p*-substituted triphenylamines, see Figure 5.

Besides the fluorescence machine, an absorption spectrophotometer (Unicam SP700), an Eppendorf photometer for fluorescence quenching experiments and a flash-photolysis setup were in use. An ESR spectrometer was available to measure triplet exciplexes. The fluorescence equipment was built up by Dieter Rehm (1962-1965). His contribution was of eminent importance for the success of the experiments in the group.

Epilogue

The present report is based on the recollection of the author over the period of 1964 through 1971, now around 40 years ago (Figure 9). Mainly the investigations carried out in Amsterdam and which were reported in a Ph.D. thesis^{12,13,25} are considered.



Figure 9. Ph.D. ceremony of the author (Free University, Amsterdam, January 1972). From left: Albert Weller, Arie Kraaijeveld, Klaas Zachariasse, and Henk Knibbe. A.K. and H.K. acted as paranymph.

Courtesy of Klaas Zachariasse

The work of the Weller group in Amsterdam was not mentioned in the recent overview of the chemical research in the Netherlands between 1945 and the early 1980s.³⁹

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