10. Free-Energy Dependence of the Ion Yield of Photo-Induced Electron-Transfer Reactions in Solution

by **Eric Vauthey***, **Paul Suppan**, and **Edwin Haselbach**

Institute of Physical Chemistry, University of Fribourg, CH-1700 Fribourg

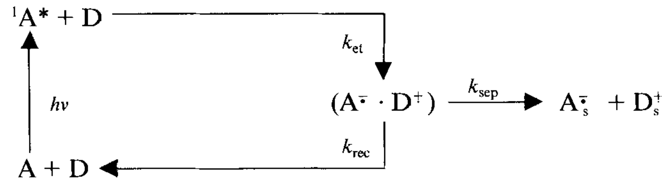
(28.IX.87)

A study of photo-induced electron-transfer reactions in MeCN with 9,10-dicyanoanthracene as acceptor and 21 electron donors with transient photoconductivity measurements is reported. The free-ion yield and the rate constant of back electron transfer are determined. For exergonic reactions, the '*Marcus*-inverted' region is observed. The fit with the theory is best, when a nearly solvent-independent *Coulomb* term is used in the calculation of the energy balance.

Introduction. – The behaviour of the rate constant of electron transfer as a function of the free energy of reaction has been investigated very intensively. Several theoretical treatments have been developed [1–5]. The rate of electron transfer is expected to be slow for weakly exergonic reactions, to increase with moderate exergonicity to a maximum, and for very exergonic processes, the rate is predicted to decrease. This fall has been called the 'inverted region'. This behaviour is analogous to the energy-gap law for radiationless transition between electronically excited states. Much experimental work has been performed to confirm this prediction. In all cases, the initial rise of the rate has been observed, but in most cases no inverted region has been detected: in the exergonic region, the rate constant keeps its maximal value, which corresponds to the diffusion rate constant [6–9]. Nevertheless, the inverted region has been observed in glassy solids [10] [11] and in rigid bichromophoric molecules [12]. Recently, it has been reported for back electron-transfer reactions in solution, within radical-ion pairs [13]: the rate constant has been calculated from the free-ion yield, which itself has been determined by measuring the concentration of scavenger, having trapped the radical cations.

In the present paper, we report on an analogous study using 9,10-dicyanoanthracene (anthracene-9,10-dicarbonitrile; **DCA**) and a sufficiently broad range of 21 electron donors in MeCN, to cover the whole range of energies. Furthermore, in our case the ion yield is determined directly by photoconductivity measurements, thus avoiding the problem of a second electron transfer to a scavenger.

Results. – The reaction scheme is the following:



The acceptor (**DCA**) is excited in the presence of the electron donor. An encounter complex or an exciplex is generated, and the electron transfer takes place to form a geminate radical-ion pair. This species can either dissociate into solvated ions (k_{sep}) or recombine to the ground state through a back electron transfer (k_{rec}). A direct observation of this last electron transfer is not possible, but its rate constant can be calculated, if the ion yield is known:

$$k_{rec} = \frac{k_{sep}(1 - \Phi_{ion})}{\Phi_{ion}} \tag{1}$$

where k_{sep} is assumed to be almost constant amounting to $k_{sep} = 5 \cdot 10^8\ s^{-1}$ in MeCN [14].

The energy balance for the forward electron transfer is:

$$\Delta G_{et} = E_{ox} - E_{red} - E^* + C \tag{2}$$

where E_{ox} is the donor oxidation potential, E_{red} the acceptor reduction potential, E^* the energy of the excited state, and C the *Coulomb* term due to the proximity of two oppositely charged particles.

In the same way, the energy balance for the back electron-transfer reaction is:

$$-\Delta G_{rec} = E_{ox} - E_{red} + C \tag{3}$$

DCA has been chosen for its low reduction potential, $E(A/A^-) = -0.98$ V *vs.* SCE [9], which allows reactions with very weak electron donors such as biphenyl (**BIP**) as well as with strong reductants such as *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (**TMPDA**). The major problem with **DCA** as electron acceptor is the very low extinction coefficient of its radical anion [15], which makes its observation by laser-flash photolysis difficult. Another way to observe the presence of radical ions is the measurement of the transient photocurrent. This approach avoids potential problems in absorption detection such as triplet-triplet or exciplex absorptions, but it does not give absolute ion yields. However, in the case of a series of similar systems in the same solvent, relative ion yields can be deduced [16]. Indeed, the molar conductivity at infinite dilution Λ°_{m} depends only on the radii of the charges (r) and on the solvent viscosity (η) [17]:

$$\Lambda^{\circ}_{m} \cdot \eta \cdot r = \text{const.} \tag{4}$$

Nevertheless, the determination of the absolute ion yield is essential to calculate the rate constant of back electron transfer. For this reason, it is necessary to relate the intensity of the photocurrent to the ion yield. To calibrate this relationship, the ion yield of the system **DCA/BIP** has been determined by laser-flash photolysis by monitoring the absorption of $\mathbf{BIP}^{+}$ at 690 nm (*Fig. 1*).

The molar decadic extinction coefficient of $\mathbf{BIP}^{+}$ has been determined from the transient absorption of the *p*-chloranil **(CA)/BIP** system [18]:

$$^3\mathbf{CA}^* + \mathbf{BIP} \rightarrow \mathbf{CA}^{\overline{\cdot}} + \mathbf{BIP}^{+}$$

The concentrations of both $\mathbf{CA}^{\overline{\cdot}}$ and $\mathbf{BIP}^{+}$ being the same and $\varepsilon^{450}(\mathbf{CA}^{\overline{\cdot}})$ being 9700 $M^{-1} \cdot cm^{-1}$[18], the extinction coefficient of $\mathbf{BIP}^{+}$ is obtained as $\varepsilon^{690}(\mathbf{BIP}^{+}) = 9960$ $M^{-1} \cdot cm^{-1}$ *(Fig. 1)*.

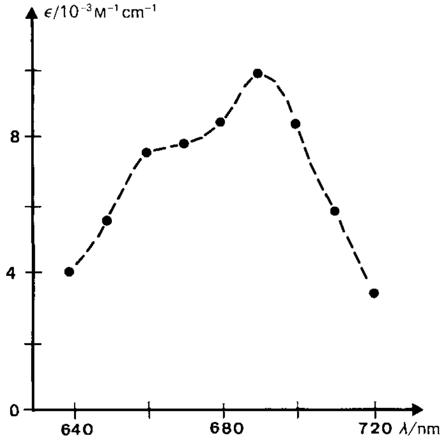


Fig. 1. *Transient spectrum of a solution of* **DCA** *and* 10^{-2} M **BIP** *in MeCN following laser-flash excitation.* The spectrum corresponds to the absorption of **BIP**$^{+}$.

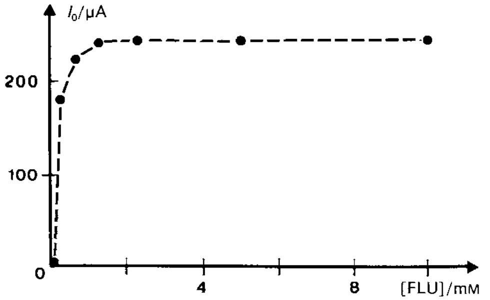


Fig. 2. *Initial transient photocurrent* I_0 *of a solution of* **DCA** *and fluorene* (**FLU**) *as a function of* [**FLU**]

The initial transient photocurrent has been measured in solutions with increasing donor concentrations, until it reached its maximal value *(Fig. 2)*. For donors with very low quenching constant k_{et}, this maximal value could not be reached, but with the knowledge of the *Stern-Volmer* constant, the photocurrent has been corrected to 100% quenching. The ion yields have been calculated by comparing the current intensity of the

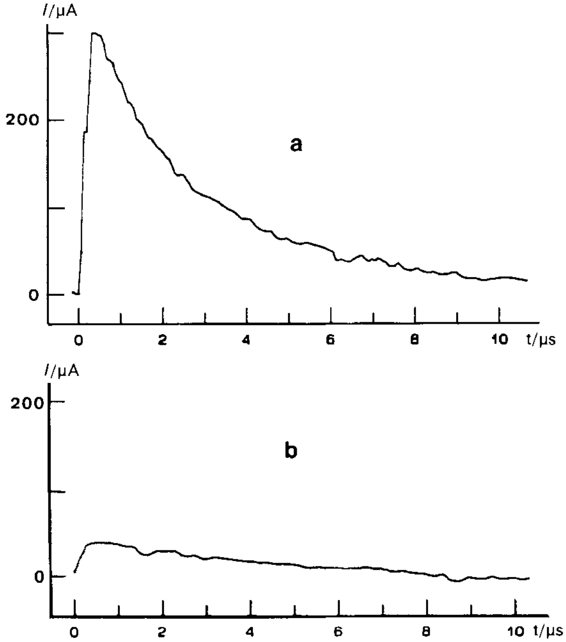


Fig. 3. *Transient photocurrent* a) *of a solution of* **DCA** *and* 10^{-2} M **BIP** in *MeCN and* b) *of a solution of* **DCA** *and* $5 \cdot 10^{-2}$ M **1,2,4-TMB** *in MeCN*

different systems with that of the **DCA/BIP** couple. The results are shown in the *Table*. For very exergonic back electron transfer, the ion yield is very significant, while it decreases with decreasing exergonicity *(Fig. 3)*. In the same way, the rate constant of back electron transfer (k_{rec}) falls with increasing exergonicity, and it is maximal for moderate exergonicity.

Table. *Ion Yield* (Φ_{ion}) *and Back Electron-Transfer Rate Constant* (k_{rec}) *for Electron-Transfer Reactions between* **DCA** *and Various Donors* (for abbreviations, see *Experimental*). In the $\Delta G'$, the *Coulomb* term is neglected. E^*(DCA) = 2.89 eV.

Donor	E_{ox} (*V vs.* SCE)	$-\Delta G'_{ct}$ [eV]	$-\Delta G'_{rec}$ [eV]	Φ_{ion} [%]	$k_{rec} 10^{-9}$ [s^{-1}]
Biphenyl	1.91 [9]	0.00	2.89	41.5	0.7
Mesitylene	1.90 [9]	0.01	2.88	21.0	1.9
p-Xylene	1.86 [9]	0.05	2.84	33.0	1.0
Anisole	1.76 [9]	0.15	2.74	11.0	4.1
Fluorene	1.65 [9]	0.26	2.63	19.4	2.1
Naphthalene	1.64 [9]	0.27	2.62	12.0	3.6
Durene	1.62 [9]	0.29	2.60	16.1	2.6
2-MN	1.52 [19]	0.39	2.50	5.7	8.3
1,3,5-TMB	1.49 [19]	0.42	2.47	3.2	15.1
1,2,3-TMB	1.42 [19]	0.49	2.40	0.8	62.0
1,4-DMB	1.34 [19]	0.57	2.32	0.2	24.5
Aniline	1.28 [16]	0.63	2.26	1.2	40.8
1,2,4-TMB	1.12 [19]	0.79	2.10	1.6	30.5
N-Methylaniline	1.03 [16]	0.88	2.01	2.0	24.5
Triethylamine	0.98 [16]	0.93	1.96	< 0.4	> 125
N,N-DMA	0.79 [19]	1.12	1.77	1.0	45.0
N,N-DEA	0.76 [19]	1.15	1.74	1.0	45.0
DABCO	0.56 [20]	1.35	1.54	2.4	20.3
2,4-DMDMA	0.53 [19]	1.38	1.51	< 0.4	> 125
3,4-DMDMA	0.43 [19]	1.48	1.41	< 0.4	> 125
TMPDA	0.16 [19]	1.75	1.14	0.8	62.0

Discussion. – Classical *Marcus* theory cannot be applied to *very* exergonic electron-transfer processes, since it predicts rate constants much smaller than those observed. This problem is avoided with a quantum-mechanical treatment. The rate constant for electron transfer between a donor and an acceptor is given by:

$$k = \frac{2\pi\,|V^2|}{h} \cdot (F.C.) \tag{5}$$

V is the matrix element describing the coupling of the electronic states of the reactants with those of the products. *(F.C.)* is the *Franck-Condon* factor [21] and is given by:

$$(F.C.) = \sum_{v=0}^{\infty} e^{-S} \cdot \frac{S^{v}}{v!} \cdot \frac{\exp[-(\Delta G^{\circ} + \lambda_{o} + vh\upsilon)^{2}/4\lambda_{o}k_{B}T]}{(4\pi\,\lambda_{o}\,k_{B}T)^{1/2}} \tag{6}$$

where υ is the mean vibration frequency of A and D involved in the process ($\tilde{\upsilon} \approx 500$–$3000$ cm^{-1}), v is the number of vibrational quanta excited in the final state, S is the electron-vibration coupling constant:

$$S = \frac{\lambda_{i}}{h\upsilon} \tag{7}$$

where λ_i is the inner-shell reorganization energy describing the change of angles and bond lengths after the electron transfer. λ_o is the outer-shell reorganization energy accompanying the re-orientation of the surrounding solvent molecules. This parameter can be treated quantum mechanically as low-frequency polarization modes of the solvent ($\tilde{\nu}_o < 100$ cm^{-1}). However, if $h\nu_o < k_BT$ as in the present case, λ_o can be described in a solvent continuum model as:

$$\lambda_o = \frac{e^2}{4\pi\varepsilon_o} \cdot \left(\frac{1}{2a_D} + \frac{1}{2a_A} - \frac{1}{r_{AD}}\right) \cdot \left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_s}\right) \tag{8}$$

where a_D and a_A are the ionic radii of the donor and the acceptor, respectively, and r_{AD} is the center-to-center distance. ε_{op} and ε_s are the optical and static dielectric constants of the solvent, respectively, with $\varepsilon_{op} \approx n^2$, n being the solvent refractive index.

The total reorganization energy is:

$$\lambda = \lambda_o + \lambda_i \tag{9}$$

When $-\Delta G^\circ$ increases at fixed λ, the rate constant k increases up to the maximum at $-\Delta G^\circ = \lambda$. For $-\Delta G^\circ > \lambda$ the rate constant then decreases (*Marcus*-inverted region). The role of the high-frequency vibrations is to absorb the reaction energy by an amount of $\mathrm{v}h\nu$ at higher vibrational levels, making the electron transfer, therefore, faster than predicted by a classical treatment operating at $\mathrm{v} = 0$ for the potential curves of reactants and products.

Fig. 4 shows the rate constant of back electron transfer for the different systems as a function of $\Delta G'_{rec}$. The continuous curve corresponds to the best fit of *Eq. 5*. In the fitting procedure, a fixed value of 0.97 eV is used for λ_o (from *Eqn. 8* with $a_{DCA} = 400$ pm and $\bar{a}_D = 380$ pm). The fit is optimal with $V = 2.9 \cdot 10^{-3}$ eV, $\tilde{\nu} = 2100$ cm^{-1}, and $\lambda_i = 0.64$ eV. These results are in general agreement with those obtained in [13] from a smaller number of less direct measurements.

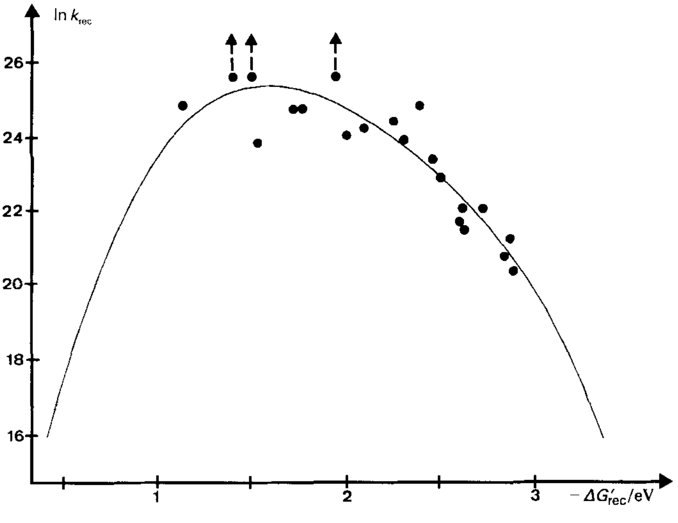


Fig. 4. *Rates of back electron-transfer reactions as a function of the exergonicity.* The points with the arrows represent lower bound values, see the *Table.*

The matrix element V for electron transfer is small as expected for these highly exergonic reactions, where the gap between the initial and the final states is very large. The value of the high frequency $\tilde{\nu} = 2100$ cm^{-1} is in good agreement with the vibrational spectrum of the molecules considered in this work. However, a value of $\lambda_i = 0.64$ eV seems to be rather large given that the precursors and the ensuing radical ions are expected to have similar structures [22]. From the algebraic form of *Eqn. 6*, it follows that increasing ΔG° would yield a lower value of λ_i in the fitting procedure. This result can be achieved by introducing a *Coulomb* term in ΔG°, hence starting the back electron transfer from the contact ion-pair stage rather than from the free ions. Using the usual *Rehm-Weller Coulomb* term of ~ -0.06 eV in MeCN [7] obviously cannot alter λ_i sufficiently. However, a substantial change occurs, if a modified *Coulomb* term [23] is used which suppresses the screening effect of the solvent between the two charges:

$$C = -\frac{1}{4\pi\varepsilon_o} \cdot \frac{e^2}{2n^2 r_{AD}} \tag{10}$$

where n is the mean refractive index of the two partners. For the different D/A couples, the mean value of this term is $C = -0.37$ eV. The fit of *Eqn. 5* yields now $\lambda_i = 0.32$ eV, which reflects better the structural properties of the present systems. In addition, it supports indirectly the validity of the modified *Coulomb* term of *Eqn. 10*.

Conclusion. – The back electron transfer which is the geminate charge recombination within the radical-ion pair formed by the initial photo-induced electron transfer is similar to an intramolecular charge transfer; it does not require the diffusional encounter of the ions, and its rate constant follows the behaviour expected in the 'inverted' region of the *Marcus-Hush* model. Within the assumption of a reasonably small value for the 'inner sphere' reorganization energy barrier for the present systems, the data are in agreement with a relatively large, nearly solvent-independent *Coulomb* term in the *Rehm-Weller* energy-balance equation.

Experimental. – **DCA** *(Kodak)*, 1,4-diazabicyclo[2.2.2]octane **(DABCO)**, *N,N,N',N'*-tetramethyl-*p*-phenylenediamine**(TMPDA)** *(Aldrich)* were sublimed. Biphenyl, fluorene, durene, 2-methoxynaphthalene **(2-MN)**, 1,3,5-trimethoxybenzene**(1,3,5-TMB)**, 1,2,3-trimethoxybenzene **(1,2,3-TMB)**, and 1,4-dimethoxybenzene **(1,4-DMB)** were recrystallized. *p*-Xylene, mesitylene, anisole, aniline, 1,2,4-trimethoxybenzene **(1,2,4-TMB)**, *N*-methylaniline, triethylamine, *N,N*-dimethylaniline **(*N,N*-DMA)**, and *N,N*-diethylaniline **(*N,N*-DEA)** were distilled using a *Fischer* column under Ar, 3,4-dimethoxy-*N,N*-dimethylaniline **(3,4-DMDMA)** and 2,4-dimethoxy-*N,N*-dimethylaniline **(2,4-DMDMA)** were synthetized according to [24]. Naphthalene (*Roth*, scintillation grade) and MeCN (UV grade) were used without further purification. All the solns. were degassed by bubbling N_2 for 10 to 15 min. (All the compounds, except those specified, are from *Fluka*.)

The laser-flash apparatus and the data acquisition system have been described earlier [25][26]. When **TMPDA**, **2,4-DMDMA**, and **3,4-DMDMA** were used, **DCA** was excited at 425 nm in order to avoid direct excitation and perhaps ionization of the electron donor. An excimer laser (*Oxford-Laser* model *KX1*) filled with a Xe, HCl, and He mixture emitting at 308 nm was used to pump a dye laser filled with a soln. of bis-MSB in EtOH, generating light at *ca.* 425 nm [27]. For all the other donors, the excitation was achieved at 355 nm with the third harmonic of a *Nd-YAG* laser (*JK Laser* model *2000*).

This work is part of Project No. 2.044–0.86 of the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung*.

REFERENCES

[1] R.A. Marcus, *J. Chem. Phys.* **1965**, *43*, 679.
[2] R.A. Marcus, *Ann. Rev. Phys. Chem.* **1964**, 155.
[3] J. Ulstrup, J. Jortner, *J. Chem. Phys.* **1975**, *63*, 4358.
[4] T. Kakitani, N. Mataga, *Chem. Phys.* **1985**, *93*, 381.
[5] R.A. Marcus, N. Sutin, *Biochim. Biophys. Acta* **1985**, *811*, 265.
[6] R.A. Marcus, *J. Phys. Chem.* **1963**, *67*, 2889.
[7] D. Rehm, A. Weller, *Isr. J. Chem.* **1970**, *8*, 259.
[8] E. Vogelmann, S. Schreiner, W. Rauscher, H. Kramer, *Z. Phys. Chem. N.F.* **1976**, *101*, 321.
[9] J. Eriksen, C. Foote, *J. Phys. Chem.* **1978**, *82*, 2659.
[10] J.V. Beitz, J.R. Miller, *J. Chem. Phys.* **1979**, *71*, 4579.
[11] J.R. Miller, J.V. Beitz, R.K. Huddleston, *J. Am. Chem. Soc.* **1984**, *106*, 5057.
[12] M.P. Irvine, R.J. Harrison, G.S. Beddard, P. Leighton, J.K.M. Sansers, *Chem. Phys.* **1986**, *104*, 315.
[13] I.R. Gould, D. Ege, S.L. Mattes, S. Farid, *J. Am. Chem. Soc.* **1987**, *109*, 3794.
[14] K. Schulten, H. Staerk, A. Weller, H.-J. Werner, B. Nickel, *Z. Phys. Chem. N.F.* **1976**, *101*, 371.
[15] E. Vauthey, P. Suppan, E. Haselbach, to be submitted for publication in *Helv. Chim. Acta.*
[16] T. Hino, H. Hakazawa, H. Masuhara, N. Mataga, *J. Phys. Chem.* **1976**, *80*, 33.
[17] P. Walden, E.J. Birr, *Z. Phys. Chem.* **1931**, *153A*, 1.
[18] R. Gschwind, E. Haselbach, *Helv. Chim. Acta* **1979**, *62*, 941.
[19] P. Iwa, U.E. Steiner, E. Vogelmann, H.E.A. Kramer, *J. Phys. Chem.* **1982**, *86*, 1277.
[20] H. Goerner, D. Schulte-Frohlinde, *Chem. Phys. Lett.* **1986**, *124*, 321.
[21] R.A. Marcus, *Faraday Discuss. Chem. Soc.* **1982**, *74*, 7.
[22] M.D. Archer, V.P.Y. Gadzekpo, J.R. Bolton, J.A. Schmidt, A.C. Weedon, *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 2305.
[23] P. Suppan, *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 509.
[24] A. Zweig, J.E. Lancaster, M.T. Neglia, W. Jura, *J. Am. Chem. Soc.* **1964**, *86*, 4130.
[25] E. Guerry-Butty, E. Haselbach, C. Pasquier, P. Suppan, D. Phillips, *Helv. Chim. Acta* **1985**, *68*, 912.
[26] M. Gremaud, P.H. Chassot, P. Suppan, *Chimia* **1983**, *37*, 379.
[27] T.F. Deutsch, M. Bass, *IEEE J. Quant. Electr.* **1969**, *4*, 260.