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Free ion yields in photoinduced electron transfer reactions from transient photoconductivity measurements: an overview[1]

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Abstract

The transient photoconductivity (TP) technique for the determination of free ion yields in bimolecular photoinduced electron transfer reactions is critically discussed. Variation of experimental parameters such as the number of charge carriers, the applied electric field, the electrode spacing, and the viscosity of the solvent confirm the theoretical predictions. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Transient photoconductivity; Free ion yields; Photoinduced electron transfer reactions

1. Introduction

Extensive theoretical as well as experimental efforts have been devoted to the understanding of photoinduced electron transfer (PET) reactions [1]. Bimolecular variants of this kind in polar solvents are of particular interest due to the ready solvation of the ions, ensuing from dissociation of the acceptor (A)/donor (D) ion pair couple (A^-/D^+) after PET Scheme 1.

The quantum yield of free ion formation, ϕ_{ion}, is a measure of the efficiency of such processes regarding charge separation. Therefore, it is of considerable practical importance in any system e.g. designed to store the energy of sunlight in form of Coulomb potential energy. However, ϕ_{ion} also provides a basis for the calculation of the rate constant of back electron transfer (k_{bet}) which opposes the rate constant (k_{sep}) of separation of the ion pair into free ions A^- and D^+. Some ten years ago, this approach has allowed the first observation of the Marcus inverted region for bimolecular PET reactions in solution [2,3]. ϕ_{ion} is given by

$$\phi_{ion} = \phi_{gip}\phi_{sep} = \phi_{gip}\frac{k_{sep}}{k_{sep} + k_{bet}} \qquad (1)$$

The yield of geminate ion pair formation, ϕ_{gip}, can be estimated from the quenching of the luminescence of the excited reaction partner, say A, according to

$$\phi_{gip} = 1 - \left(\tau_0 k_q[D] + 1\right)^{-1} \qquad (2)$$

where $[D]$ is the quencher concentration, τ_0 the luminescence lifetime of A without quencher, and k_q the quenching rate constant. Control of $[D]$ allows adjusting ϕ_{gip}. Therefore, ϕ_{sep} is calculable if ϕ_{ion} can be determined.

The most often used technique to determine ϕ_{ion} is based on the absorption of the transient free ions (TA method). However, this approach is not free of problems:

- the optical absorptions of many ions have small extinction coefficients, rendering their observation problematic, especially in the case of low ϕ_{ion},
- the absorptions of a free ion, and of this ion embedded in the geminate ion pair are very similar. Hence, it is difficult to distinguish them optically,
- the optical spectra of the ions are often not available. To circumvent this problem a secondary donor of lower oxidation potential was sometimes employed which accepts the primary hole from D^+, resulting in an ion whose spectrum is now known.

Unfortunately, this strategy opens further questions:

1. the secondary donor must be employed in high concentration to assure 100% yield of bimolecular hole exchange (i.e. it must intercept all primary hole carriers D^+). But this changes the dielectric properties of the medium on which ϕ_{ion} i.a. depends,
2. it must be assumed that the hole transfer efficiency is unity.

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[1] Dedicated to the memory of our PhD supervisor, colleague and friend Paul Suppan (1938–1998) who infected us with his enthusiasm for photochemistry and built the foundations on which the present work rests.

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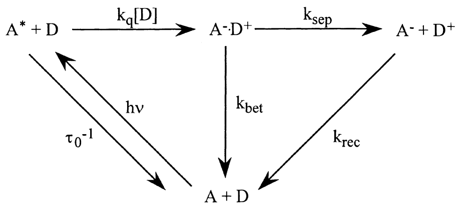

Scheme 1.

The transient photoconductivity technique (TP) provides a valuable alternative to TA for arriving at ϕ_{ion}: the generation of charged intermediates increases the conductivity of the solution which can be followed by standard techniques. Admittedly, the identity of the charge carriers is not revealed. On the other hand, a PET mechanism can be established in this way. TA does not offer this insight, given that transient absorptions can also arise from electrically neutral intermediates of unknown constitution formed via photohomolysis.

For both techniques, it is assumed that the maxima of absorption or photocurrent signals, respectively, reflect the correct ion yield. This assumption is reasonable as quenching and charge separation are very fast processes. In contrast, the diffusion controlled second order recombination of free ions is much slower, given that their (equal) concentrations are small compared to $[D]$.

2. Theory

Fast electrical conductance measurements in solution for the detection of charged intermediates were first reported in the 1960s by Kawada and Jarnagin [4] who observed photocurrents following bimolecular encounters of phenanthrene and anthracene triplets in THF solution. Shortly afterwards, several groups started to exploit this technique: Beck and coworkers [5] for the detection of pulse-radiolytically formed ions, Albrecht and Pilloff [6] for investigating the biphotonic ionisation of amine donors, and Mataga and coworkers [7] for following buildup and decay of PET-produced ions.

During the last 25 years several other groups have demonstrated the value of TP [8–18]. Despite this, only few researchers presently apply this simple and straightforward technique for the determination of ϕ_{ion}. TA is mostly preferred – despite all disadvantages it bears, as described above. Therefore, we will discuss in this article the TP technique in detail and show its suitability for the study of ϕ_{ion} in PET reactions.

2.1. Origin of the electrical signals

Although several designs of TP measurements are possible (see references quoted above), we will focus on the simplest possible setup whose electric scheme is shown in Fig. 1.

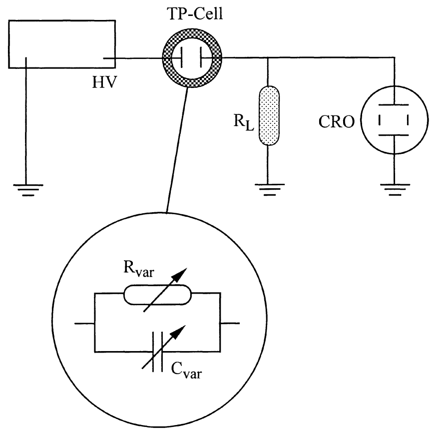

Fig. 1. Electric circuit of the transient photoconductivity (TP) setup. HV, high voltage; R_{L}, anodic load; CRO, oscilloscope; R_{var}, variable resistor; C_{var}, variable capacity.

The high voltage power supply creates an electric field between the electrodes of the photocurrent cell. If ions are formed by photoexcitation, a drop of voltage is recorded through an anodic load operating in parallel to an oscilloscope.

The cell can be electrically divided into two components: a variable resistor, and a variable capacity. Generation of ions between the electrodes changes the specific resistance and the relative dielectric constant. The following theoretical development is a modification of the approach reported by Leo [19] for the so-called 'cylindrical proportional counter'.

2.1.1. Currents due to free ions

The electrodes of the cell form a capacitor (approximated by a plate capacitor). If a charge q is placed at distance x from one of the plates, its potential energy E_{pot} is given by

$$E_{\mathrm{pot}} = q\varphi(x) \tag{3}$$

the potential being defined as

$$\varphi(x) = \int_x^{\infty} E\,\mathrm{d}x \quad \text{with} \quad \varphi(\infty) = 0 \tag{4}$$

If the charge moves by $\mathrm{d}x$, $\mathrm{d}E_{\mathrm{pot}}$ is

$$\mathrm{d}E_{\mathrm{pot}} = q\frac{\mathrm{d}\varphi(x)}{\mathrm{d}x}\,\mathrm{d}x \tag{5}$$

The electric field E between the electrodes is given by

$$E = \frac{Q}{\varepsilon_{\mathrm{r}}\varepsilon_0 S} \quad \text{with} \quad Q = C \times U \quad \text{and} \quad C = \varepsilon_{\mathrm{r}}\varepsilon_0 \frac{S}{d} \tag{6}$$

where S is the electrode surface area, C the capacity, U the applied voltage, Q the total charge on the plates (with spacing d), ε_{r} the relative permittivity, and ε_0 the vacuum permittivity.

A charged capacitor has the potential energy

$$E_{\text{pot}} = \frac{1}{2}CU^2 = \frac{1}{2}\frac{Q^2}{C} \quad \text{and} \quad \mathrm{d}E_{\text{pot}} = \frac{Q}{C}\mathrm{d}Q \tag{7}$$

Substitution and integration yields

$$\mathrm{d}E_{\text{pot}} = \frac{Q}{C}\,\mathrm{d}Q = q\frac{\mathrm{d}\varphi(x)}{\mathrm{d}x}\,\mathrm{d}x$$

$$\mathrm{d}Q = \frac{qC}{Q}\int_{x}^{x+\mathrm{d}x}\frac{\mathrm{d}\varphi(x)}{\mathrm{d}x}\cdot\mathrm{d}x = \frac{qC}{Q}\left[-\frac{Q}{\varepsilon_{\mathrm{r}}\varepsilon_0 S}\,x\right]_{x}^{x+\mathrm{d}x} \tag{8}$$

An electric field E forces a charge to move with time dependant velocity $v(t)$

$$v(t) = \frac{\mathrm{d}x}{\mathrm{d}t} \tag{9}$$

which results in the observable current $i(t)$ (i.e. the TP current)

$$i(t) = \frac{\mathrm{d}Q}{\mathrm{d}t} = -\frac{qv(t)}{d} \tag{10}$$

Eq. (10) can be dissected into currents due to n^+ positive and n^- negative charge carriers at time t

$$i(t) = i^-(t) + i^+(t) = \frac{n^-(t)qv^-}{d} + \frac{n^+(t)qv^+}{d} \tag{11}$$

The final velocity of the charges in a solvent of viscosity η can be calculated on the basis of the following differential equation, valid for dilute solutions

$$m\frac{\mathrm{d}v}{\mathrm{d}t} = qE - 6\pi\eta r v(t) \tag{12}$$

where m is the mass of the charged species, and r its radius (its shape being assumed as spherical).

From the Stokes model, the total force acting on the charge is due to its attraction by the oppositely charged electrode (migration), from which the force due to laminar friction is subtracted

$$v(t) = \left(v_0 - \frac{qE}{6\pi\eta r}\right)\exp\left[-\frac{6\pi\eta r}{m}\,t\right] + \frac{qE}{6\pi\eta r} \tag{13}$$

with

$$v_0 = v(t_0) = 0 \tag{14}$$

and

$$v(t\to\infty) = \frac{qE}{6\pi\eta r} \tag{15}$$

It is reasonable to assume that 99% of the final velocity is attained at time t_{99}. Hence,

$$t_{99} = \frac{m}{6\pi\eta r}\ln(100) \tag{16}$$

Taking $q = 1.602\times10^{-19}$ C, and typical values e.g. for benzophenone (BP) in acetonitrile (MeCN): $E = U/d = 500\,\mathrm{V}/0.006\,\mathrm{m}$, $\eta = 0.325.10^{-3}\,\mathrm{kg\,m^{-1}\,s^{-1}}$, $r = 3.36.10^{-10}\,\mathrm{m}$, $m = 3.02.10^{-25}$ kg, then Eq. (16) yields $t_{99} = 6.76.10^{-13}$ s. Hence, within the timescale of the experiment the velocity from Eq. (15) can be assumed as constant, its value being $v(t\to\infty)$ =$6.49\times10^{-3}\,\mathrm{m\,s^{-1}}$. Finally, the ion mobility μ is defined by

$$v = \mu E \tag{17}$$

which leads with Eq. (15) to

$$\mu = \frac{q}{6\pi\eta r} \tag{18}$$

Eq. (11) can be rewritten to yield the final conductivity equation [20]

$$i(t) = \frac{n(t)q(\mu^- + \mu^+)E}{d} = \frac{n(t)q^2E}{6\pi\eta d}\left(\frac{1}{r^-} + \frac{1}{r^+}\right) \tag{19}$$

It follows that the observed TP $i(t)$ is proportional to $n(t) = n^-(t) = n^+(t)$, i.e. to the number of formed ions, to the applied electric field E (or via Eq. (6) to the applied voltage U), and to the sum of the reciprocal radii of anion (r^-) and cation (r^+), respectively. On the other hand, TP is indirectly proportional to the electrode spacing d and to the viscosity η.

As current is defined as amount of charge moving per unit time, all origins of charge movements contribute to the observed current – including diffusion and convection. According to Herzfeld [21], diffusion can be neglected when the electrical potential energy in the system is much larger than the thermal energy $k_{\mathrm{B}}T$, a condition which is normally fulfilled (in our set-up by a factor of 20 000). Convection, which is due to density alterations in the system, is also negligible in the actual time scale.

2.1.2. Currents due to dipolar contribution

In some cases, photocurrents originating from photoionisation were observed in nonpolar solvents [22–27]. Normally, ion solvation is unfavourable in such media. If no ionisation upon photoexcitation occurs, then currents due to dipole moment changes and rotational reorientation of dipoles are observable. Dipole moments of several excited molecules and exciplexes were determined with this technique by Braun, Smirnov and coworkers [28–31]. In a first approach, they considered only fast rotating dipoles and neglected polarisation effects of the solvent [32]. In a subsequent treatment, they also included the latter term [33]. We note that their mathematical treatment is only applicable to nonpolar solvents. However, knowledge of the weight of dipolar effects with respect to ionic conduction is essential for PET reactions which occur mostly in polar solvents and involve dipolar intermediates such as ion pairs and exciplexes.

2.2. Additional remarks

The TP technique applied to PET related problems measures the change in conductivity of a sample when it is excited by a flash of light. This is due to the generation of (new) charge carriers and to their ensuing reactions such as recombination or further ET reaction, e.g. with oxygen [16]. Sometimes, PET induced TP currents cross the 'dark' conductivity baseline and 'negative' currents are observed. This indicates that in the course of the secondary reactions the nature of the charge carriers and hence their mobility changes [15].

3. Experimental

3.1. TP setup

Our basic experimental design consisted of a classical laser flash photolysis system (19 ns pulsewidth) which is described elsewhere [17]. The laser intensity at 355 nm was controlled through chemical filters (aqueous $NaNO_2$ solutions) and monitored by a calibrated photodiode which allowed normalisation of the photocurrents.

A new type of TP cell was used in this study as shown in Fig. 2, whose electrical setup corresponds to that shown in Fig. 1.

This cell allows variation of the inter-electrode spacing from 0.002–0.018 m. Typically, a voltage of 500 V was applied for a spacing of 0.006 m. With our recording system (Gould 4074, 100 MHz; Tektronix TDS 620A, 500 MHz) and an anodic load of 50 Ω, a time resolution of a few ns was obtained. The samples were either deoxygenated by argon bubbling (when using the cell of Fig. 2), or degassed by the freeze-pump-thaw-shake procedure (cell employed in [17]).

In order to avoid degradation of the solution, the electric field was applied only for a short time, and only single shot measurements were performed. Such TP measurements exhibit a peak error of less than 5% for a 2σ confidence limit (σ = standard deviation). As between different A/D systems the TP is comparable only for similar ϕ_{gip}, the quencher concentrations were always adjusted to obtain typically $\phi_{\mathrm{gip}} = 0.99$. Linear extrapolation from lower ϕ_{gip} to $\phi_{\mathrm{gip}} = 1$ is not recommended as errors of several percents can result [34]. The sensitivity of the TP method can be estimated through Eq. (19): In a TP cell of 'active' volume = 1.7×10^{-4} dm^3 such as the one described in [17], and for ions with $r^- = r^+ = 3.5 \times 10^{-10}$ in the solvent MeCN, a current of 1 μA corresponds to a total ion concentration of about 6×10^{-8} M.

3.2. Chemicals

All chemicals used were of the best available quality. They were further purified if necessary. Abbreviations used are: Biphenyl (BiP), benzophenone (BP), 1,4-diazabicyclo[2.2.2]octane (DABCO), 9,10-dicyanoanthracene (DCA), *N,N*-dimethylaniline (DMA), 4-dimethylamino-4′-cyanostilbene (DMACS), acetonitrile (MeCN), *N,N*-dimethylformamide (DMF), dimethylsulfoxide (DMSO).

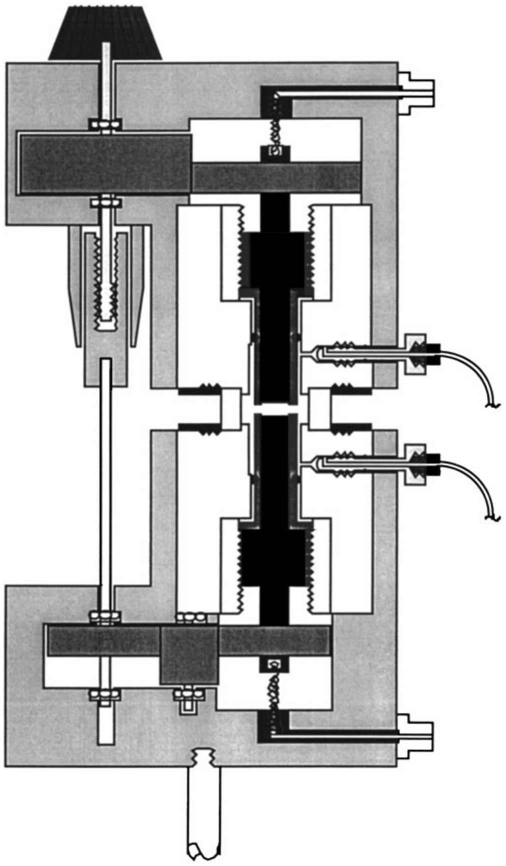

Fig. 2. TP cell with adjustable electrode spacing. The electrodes (black) are made from stainless steel and are covered by a thin platinum layer. The main body (PVDF) is surrounded by an aluminium shield. Excitation and optical observation of the transients is performed through four quartz windows, arranged perpendicularly to the electrodes. The spacing of the electrodes is controlled by a micrometric screw and can be changed from 0.002–0.018 m.

4. Results and discussion

4.1. TP as a function of the factors in Eq. (19)

Eq. (19) predicts that the observed TP depends on instrumental parameters, the viscosity of the solvent, the number of charge carriers, and the molecular properties of the A/D system. Several experiments were designed to validate it by isolating each factor which allows to investigate the response of TP upon a corresponding change. The well studied system BP/DABCO in MeCN [35] was chosen as an ideal substrate for these investigations, given that its ϕ_{ion} is essentially unity [36,37].

4.1.1. Number of charge carriers

In order to test the influence of the number of free ions $n(t)$ on the TP signal of the BP/DABCO/MeCN system, the intensity of the laser excitation was varied. As the yield of triplet BP (^{3}BP) as well as the global ion yield are unity, the current should vary linearly with laser intensity. However, it is known, that the absorbance of ^{3}BP tends to saturate

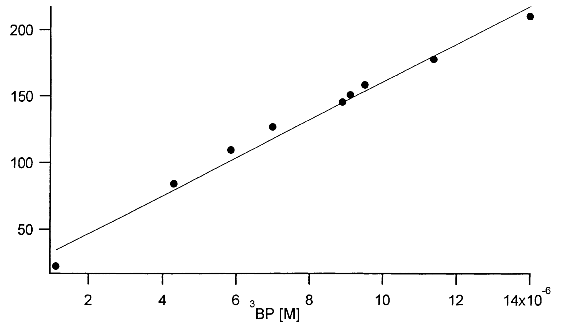

Fig. 3. TP as a function of the molar concentration of triplet benzophenone [^{3}BP] for BP/DABCO/MeCN ($A_{\mathrm{BP,\ 355\ nm}} = 1$, [DABCO] = 0.02 M, $\phi_{\mathrm{gip}} = 0.99$, $\phi_{\mathrm{ion}} = 1$). Note that the total number n of free ions is directly proportional to [^{3}BP].

under such conditions [17]. Therefore, the observed peak TP is plotted in Fig. 3 against [^{3}BP] which was determined in a control experiment under the same conditions via its transient absorption (^{3}BP has an extinction coefficient of 6500 $\mathrm{M}^{-1}\ \mathrm{cm}^{-1}$ at 525 nm [17]). A linear behaviour was observed as predicted by Eq. (19).

4.1.2. Applied voltage *U*

The operating electric field E varies linearly with the applied voltage U. Hence, keeping the other variables constant, the observed TP should vary linearly with U. Fig. 4 clearly reflects this behaviour.

In order to account for a possible enhancement of the ionic dissociation mechanism due to the action of the electric field E (Wien effect), a system with $\phi_{\mathrm{ion}} < 1$ must be examined: this opens the possibility to observe a more than linear increase of TP above a certain threshold of E, resulting from a corresponding increase of ϕ_{ion}. We chose as test system DCA/BiP/MeCN with $\phi_{\mathrm{ion}} = 0.5$ [36] whose TP trace is shown in Fig. 7. Fig. 4 shows that also here Eq. (19) is perfectly satisfied and no deviation from linearity occurs. Note that our applied electrical field E is relatively small for an observation of the Wien effect, compared to those fields of the order 10^4–10^5 V cm^{-1} where it could be observed [38].

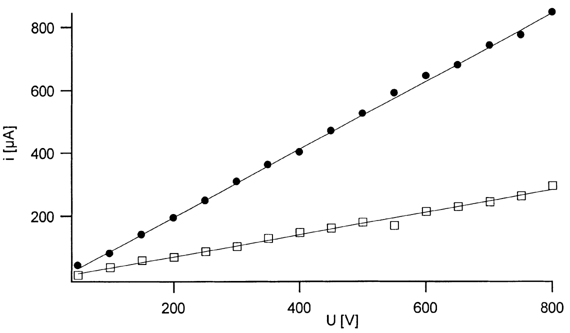

Fig. 4. TP as a function of the applied voltage U. (•): BP/DABCO/MeCN ($A_{\mathrm{BP,\ 355\ nm}} = 1$, [DABCO] = 0.02 M, $\phi_{\mathrm{gip}} = 0.99$, $\phi_{\mathrm{ion}} = 1$); (□): DCA/BiP/MeCN ($A_{\mathrm{DCA,\ 355\ nm}} = 1$, [BiP] = 0.3 M, $\phi_{\mathrm{gip}} = 0.93$, $\phi_{\mathrm{ion}} = 0.49$). Laser intensity and electrode spacing are slightly different for the two sets of measurements.

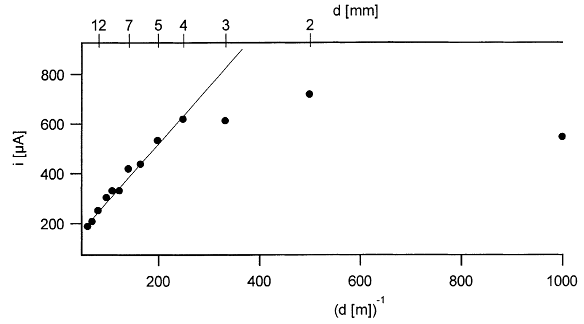

Fig. 5. TP as a function of the (reciprocal) electrode spacing d for BP/DABCO/MeCN ($A_{\mathrm{BP,\ 355\ nm}} = 1$, [DABCO] = 0.02 M).

4.1.3. Electrode spacing *d*

In order to keep our electric field E constant upon variation of the electrode spacing d, an applied voltage $U = dE$ was chosen which results in the prediction of indirect proportionality between observed TP and d. This is experimentally confirmed as shown in Fig. 5 for the system BP/DABCO/MeCN. The deviation from linearity at small d is readily explained: the laser beam exhibits a diameter of 6 mm. Hence, an increasing amount of excitation intensity is lost upon closing up the electrodes.

4.1.4. Solvent viscosity η

As Eq. (19) is based on the hydrodynamic model of Stokes, an indirect proportionality between peak current and viscosity is expected. Unfortunately, the situation is more complex as diffusion is slowed down with rising viscosity. Hence, diffusion controlled rates may decrease which may affect in turn ϕ_{ion}. Even ET rates may change as solvent relaxation is also viscosity dependant.

Viscosity can be either varied by temperature (for the same solvent), or by the choice of different solvents. The first variant has the disadvantage that a change in temperature also influences the intrinsic rate constants. The second variant is restricted by the limited choice of suitable solvents: in order to be comparable, they all need to be of similar polarity, as well to be chemically inert with respect to the reactants.

To shed light on these questions, the system pyrene/DMA [39] with $\phi_{\mathrm{ion}} = 0.99$ in MeCN [40] was investigated. Table 1 shows the choice of the solvents with the appropriate relevant parameters of the A/D system. The Born polarity function $f(\varepsilon_r) = (1 - 1/\varepsilon_r)$ which is a measure of the solvation of ions, is larger than 0.97 for all solvents.

We note that the quenching efficiency decreases with increasing viscosity, and that a decrease of only 5% in ϕ_{ion} is expected from ϕ_{gip}. Hence, we can safely predict that the decrease of the peak TP by two orders of magnitude on passing from MeCN to 1,3-propanediol, is essentially due to the viscosity effect, and that TP therefore must exhibit a

Table 1
Physicochemical parameters and experimental results for pyrene/DMA in solvents of different viscosity

Solvent	ε_r[a]	T (°C)[a]	$f(\varepsilon_r)$[b]	η^{-1}[c] (cP^{-1})	τ_0[d] (ns)	k_{SV}[e] (M^{-1})	$k_q \times 10^9$ (M^{-1} s^{-1})	ϕ_{gip}[f] (%)
MeCN	37.5	20	0.973	2.762	125	630	5.04	99.2
DMF	36.7	25	0.973	1.082				
DMSO	46.7	25	0.979	0.501	320	762	2.40	99.3
1,2-ethanediole	37.7	25	0.973	0.038	380	159	0.42	97.0
1,3-propanediole	35.0	20	0.971	0.021	390	91	0.23	94.7

[a] From [44].

[b] Born's polarity function.

[c] From [44]. $T = 20$°C, except for 1,2-ethanediole (15°C).

[d] Measured for pyrene after deoxygenation by argon bubbling for 10 min. Two decays (fast and slow) are observed for higher viscosity.

[e] Stern–Volmer plots for higher viscosities are not linear.

[f] Calculated for [DMA] = 0.2 M on the basis of Eq. (2).

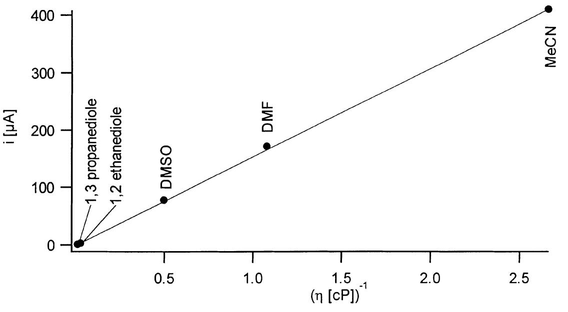

Fig. 6. TP as a function of the reciprocal viscosity η for different polar solvents, which all exhibit Born functions $f(\varepsilon) > 0.97$. The D/A system is pyrene/DMA ($A_{\text{pyrene, 355 nm}} = 0.5$, [DMA] = 0.2 M, $\phi_{gip} = 0.99$).

linear correlation with (reciprocal) viscosity. This is born out by experiment as shown in Fig. 6.

4.1.5. Ion radius r

Eq. (19) shows that the same TP for two different A/D systems can only be expected when – all other parameters being equal – both exhibit the same sum of reciprocal ionic radii, which is rarely the case. Table 2 shows the consequences of this type of non-equivalency on TP for the three presently employed A/D systems. The relevant radii are estimated by the simple spherical model

$$r = 0.5\left(\frac{M_w}{\delta N_A}\right)^{1/3} \tag{20}$$

with δ being the density of the substrates (set uniformly to unity), and M_w their molecular mass. Note that we assume: $r^- = r_A$ and $r^+ = r_D$. For molecules differing very much from spherical shape (e.g. porphyrins), corrections can be applied [8].

From Table 2, we recognize that for systems of the present kind exhibiting comparable size, the radii effect leads to only a few percent in TP variation. Its influence diminishes even further when the radii are calculated including the first ionic solvation shell (i.e. a concept taken from electrochemistry [20,38]): in view of the algebraic nature of the r-term in (19) differential effects between two A/D systems fall off rapidly with increasing radii.

4.2. TP influenced by factors outside Eq. (19)

4.2.1. Dipolar contributions

As discussed in the theoretical section, rotating dipoles can contribute to TP which was examined by Braun, Smirnov and coworkers [28,29,31,32,41] in two distinct ways. Firstly, molecules were excited to a state with strong charge transfer character, or secondly exciplexes were formed by quenching reactions in nonpolar solvents. Along both routes, large dipole moments were created upon excitation which lead to TP effects.

However, given the short lifetime of the excited states this phenomenon is expected to occur in the ns-timescale, i.e. out of reach of our instrumental setup for the determination of ϕ_{ion}. We examined this question along the two ways indicated above: firstly, by exciting 4-dimethylamino-4′-cyanostilbene (DMACS) in hexane which has excited state properties similar to 4-dimethylamino-4′-nitrostilbene (lifetime, and dipole moment in the excited state of 2.8 ns and 23.3 D, respectively [28,32]); and secondly, by quenching

Table 2
Influence of ion size on the transient photoconductivity (TP) of three different A/D systems[a]

A/D couple	r_A (10^{-10} m)	r_D (10^{-10} m)	$1/r_A + 1/r_D$ (10^9 m)	Relative TP (%)
BP/DABCO	3.36	2.85	6.49	100
DCA/BiP	3.62	3.17	5.92	91
Pyrene/DMA	3.47	2.93	6.29	97

[a] All other factors being equal.

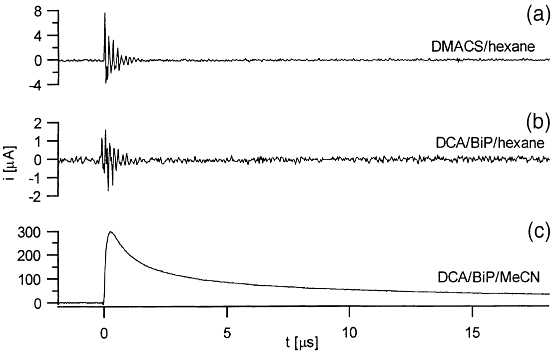

Fig. 7. Currents due to dipolar contributions in apolar solvents: DMACS in hexane ($A_{355\ \mathrm{nm}} = 0.42$) (a); DCA/BiP/hexane ($A_{\mathrm{DCA},\ 355\ \mathrm{nm}} = 0.3$, [BiP] = 0.27 M) (b). The TP trace for DCA/BiP/MeCN ($A_{\mathrm{DCA},\ 355\ \mathrm{nm}} = 1$, [BiP] = 0.3 M) is shown for comparison (c).

the fluorescence of DCA by BiP in hexane which results in an exciplex emission at $\lambda_{\max} = 450$ nm [42]. For similar exciplexes, lifetimes and dipole moments of a few ns and of several debyes, respectively, were reported [31,43]. In accordance with the expectation above no TP was observed in both cases as shown in Fig. 7 (the signals at $t = 0$ are due to noise due from the interference of the electrical circuit with the pockels cell of the laser).

4.2.2. Concentration

Kohlrausch showed that the molar conductivity Λ_X depends in a nonlinear fashion on the molar concentration of the electrolyte X

$$\Lambda_X = \Lambda_0 - K\sqrt{X} \tag{21}$$

where K is a constant. Transformation of Eq. (21) shows that also the observed current i is dependant on the concentration of X

$$i = \Lambda_X SEX = \left(\Lambda_0 - K\sqrt{X}\right)SX \tag{22}$$

the symbols S and E being defined in Eq. (6).

This effect is not observed under our conditions as shown in Fig. 3, which exhibits a linear correlation. We conclude that our ion concentrations are too low for a manifestation of this effect.

4.2.3. Temperature

Temperature changes influence the presently relevant factors: viscosity and reaction rates. Therefore, it is important to control the temperature during the TP measurements. Unfortunately, several heat sources of a priori unknown importance exist: (1) from the current flow through the solution, (2) from the internal conversion of excited species, and (3) from the absorption of the IR-part of the monitoring light by the solvent if TA is performed simultaneously with TP. The answers to these questions are:

1. The temperature rise ΔT is proportional to the input energy E_{input}, $C_{\mathrm{p,sol}}$ being the heat capacity and m_{sol} the mass of the solution between the electrodes

   $$\Delta T = \frac{E_{\mathrm{input}}}{C_{\mathrm{p,sol}} m_{\mathrm{sol}}} \tag{23}$$

   For the current flow, the electric energy is given by

   $$E_{\mathrm{input}} = \frac{U^2}{R_{\mathrm{sol}}}\Delta t \quad \text{with} \quad R_{\mathrm{sol}} = \frac{U - R_L i}{i} \tag{24}$$

   For MeCN with $C_{\mathrm{p,sol}} = 2.23\ \mathrm{kJ\,kg^{-1}\,K^{-1}}$ [44] and $m_{\mathrm{sol}} = 2.34.10^{-4}$ kg, and inserting typical electrical parameters of $U = 500$ V, $i = 100\ \mu$A and $R_{\mathrm{L}} = 50\ \Omega$, we obtain a temperature rise of 0.1 K for an electrical current pulse of 1 s
2. Temperature rise resulting from internal conversion can be estimated as 0.01 K per laser pulse
3. Unwanted IR absorption from the monitoring light can be avoided by using appropriate filters. The conclusion is that under our conditions essentially constant temperature conditions prevail. It is strengthened by taking fast heat dissipation into account. Nevertheless, prolonged application of high voltage and light irradiation to the solutions should be avoided to prevent their electrolysis and photolysis, respectively.

5. Conclusions

In this paper, we have summarised in detail our positive experience with the transient photoconductivity (TP) technique to establish ϕ_{ion}. Results obtained with TP are highly reproducible and were confirmed, where possible, by other techniques such as the transient thermal phase grating [36,37] or the transient absorption (TA) technique [40]. As discussed in the introduction, TP is free from the ambiguities accompanying TA. A simple theoretical model allows to interpret the TP signals. With our simple instrumentation, preliminary information on ϕ_{ion} can be collected within a very short time. We are convinced that many workers engaged in PET research, may wish to integrate TP in their instrumental outfit. We are ready to provide more details about our experiences.

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References

[1] M.A. Fox, M. Channon, Photoinduced Electron Transfer, Elsevier, Amsterdam, 1988.

[2] I.R. Gould, D. Ege, S.L. Mattes, S. Farid, J. Am. Chem. Soc. 109 (1987) 3794.
[3] E. Vauthey, P. Suppan, E. Haselbach, Helv. Chim. Acta 76 (1988) 1319.
[4] A. Kawada, R. Jarnagin, J. Chem. Phys. 44 (1966) 1919.
[5] G. Beck, Int. J. Radiat. Phys. Chem. 1(3) (1969) 361.
[6] H.S. Pilloff, A.C. Albrecht, J. Chem. Phys. 49 (1968) 4891.
[7] Y. Taniguchi, Y. Nishina, N. Mataga, Bull. Chem. Soc. Jpn. 45 (1971) 764.
[8] S.G. Ballard, D.C. Mauzerall, J. Chem. Phys. 72(2) (1980) 933.
[9] D. Mauzerall, S.G. Ballard, Ann. Rev. Phys. Chem. 33 (1982) 377.
[10] S.G. Ballard, Rev. Sci. Instrum. 47(9) (1976) 1157.
[11] K. Sun, D. Mauzerall, J. Phys. Chem. B 102 (1998) 6440.
[12] R. Gschwind, E. Haselbach, Helv. Chim. Acta 62 (1979) 941.
[13] H.G. Klever, Ph.D. Thesis, University of Bochum, 1974.
[14] R. Kuhlmann, W. Schnabel, J. Photochem. 7 (1977) 287.
[15] F. Elisei, G. Favaro, H. Görner, J. Photochem. Photobiol. A: Chem. 59 (1991) 243.
[16] M. von Raumer, A. Sarbach, P. Suppan, J. Photochem. Photobiol. A: Chem. 107 (1997) 43.
[17] M. von Raumer, P. Suppan, P. Jacques, J. Photochem. Photobiol. A: Chem. 105 (1997) 21.
[18] M. von Raumer, P. Suppan, E. Haselbach, Chem. Phys. Lett. 252 (1996) 263.
[19] W.R. Leo, Techniques for Nuclear and Particle Physics Experiments, A How-to Approach, Springer, Berlin, 1987.
[20] R.G. Compton, G.H.W. Sanders, Electrode Potentials, Oxford Science Publications, Oxford, 1996.
[21] K.F. Herzfeld, Phys. Rev. 34 (1926) 791.
[22] M.C. Sauer Jr., A.D. Trifunac, R. Cooper, D. Meisel, Chem. Phys. Lett. 92 (1982) 178.
[23] M.C. Sauer Jr., K.H. Schmidt, A. Liu, J. Phys. Chem. 91 (1987) 4836.
[24] M.C. Sauer, I.A. Shkrob, J. Yan, K. Schmidt, A.D. Trifunac, J. Phys. Chem. 100 (1996) 11325.
[25] K.H. Schmidt, M.C. Sauer Jr., Y. Lu, A. Liu, J. Phys. Chem. 94 (1990) 244.
[26] L.V. Lukin, A.V. Tolmachev, B.S. Yakovlev, Chem. Phys. Lett. 99 (1983) 16.
[27] B.S. Yakovlev, L.V. Lukin, in: K.P. Lawley (Ed.), Photodissociation and Photoionization, Wiley, New York, 1985.
[28] S.S. Brown, C.L. Braun, J. Phys. Chem. 95 (1991) 511.
[29] K.N. Grzeskowiak, S.N. Smirnov, C.L. Braun, J. Phys. Chem. 98 (1994) 5661.
[30] S.N. Smirnov, C.L. Braun, S.R. Greenfield, W.A. Svec, M.R. Wasielewski, J. Phys. Chem. 100 (1996) 12329.
[31] K.N. Grzeskowiak, S.E. Ankner-Mylon, S.N. Smirnov, C.L. Braun, Chem. Phys. Lett. 257 (1996) 89.
[32] S.N. Smirnov, C.L. Braun, J. Phys. Chem. 96 (1992) 9587.
[33] S.N. Smirnov, C.L. Braun, J. Phys. Chem. 98 (1994) 1953.
[34] M. von Raumer, Ph.D. Thesis, University of Fribourg/CH, 1996.
[35] E. Haselbach, P. Jacques, D. Pilloud, P. Suppan, E. Vauthey, J. Phys. Chem. 95 (1991) 7115.
[36] A. Henseler, E. Vauthey, J. Photochem. Photobiol. A: Chem. 91 (1995) 7.
[37] E. Vauthey, A. Henseler, J. Photochem. Photobiol. A: Chem. 112 (1998) 103.
[38] G. Kortüm, Lehrbuch der Elektrochemie, VCH, Weinheim, 1957.
[39] N. Mataga, Y. Hirata, Y. Kanda, J. Phys. Chem. 87 (1983) 1659.
[40] N. Mataga, T. Asahi, Y. Kanda, T. Okada, T. Kakitani, Chem. Phys. 127 (1988) 249.
[41] S.N. Smirnov, C.L. Braun, Chem. Phys. Lett. 217 (1994) 167.
[42] E. Vauthey, private communication.
[43] S.E. Mylon, S.N. Smirnov, C.L. Braun, J. Phys. Chem. A 102 (1998) 6558.
[44] J.A. Ridick, W.B. Bunger, Organic Solvents, Wiley Interscience, New York, 1970.