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KOCH, Marius, et al.

Abstract

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Reference


DOI : 10.1021/ja208265x

Available at:
http://archive-ouverte.unige.ch/unige:18737

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Bimolecular Photoinduced Electron Transfer in Imidazolium-Based
Room-Temperature Ionic Liquids Is Not Faster than in Conventional
Solvents

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Supporting Information

ABSTRACT: The fluorescence quenching of 3-cyanoperylene upon
electron transfer from N,N-dimethylaniline in three room-temperature
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controlled by the solvent dynamics in both cases, being slower in the RTILs than in the conventional organic solvent of similar
viscosity, and (iii) the previously reported reaction rates much larger than the diffusion limit at low quencher concentration in
RTILs originate from a neglect of the static and transient stages of the quenching, which are dominant in solvents as viscous as
RTILs.

INTRODUCTION

The interest in room-temperature ionic liquids (RTILs) as
nonvolatile, thermally stable, and conductive solvents has
undergone an impressive increase over the past few years.1−4
These properties, together with the broad electrochemical
window and a very good solubility for both organic and
inorganic solutes, have turned RTILs into promising alter-
natives to "conventional" solvents in fields as diverse as organic
synthesis2,4 or solar energy conversion.3,5−7

Besides these potential applications, many efforts have been
made to obtain a deeper understanding of the possible intrinsic
differences of elementary processes in ionic and conventional
liquids.5,9 In particular, electron transfer (ET), constituting the
simplest and, at the same time, one of the most ubiquitous
chemical reactions, has been the subject of studies yielding
surprising and unexpected results. Intramolecular ET reactions
have not been found to show any markedly different behavior in RTILs than in conventional solvents,10−12 whereas just the
opposite was reported for their bimolecular analogues. Most of
the previous works on ET in RTILs reported extremely accelerated reaction rates compared to conventional sol-
vents.13−18 Indeed, the ET reactions in conventional solvents
were observed to be diffusion controlled, while quenching rate
constants up to 2 orders of magnitude larger than diffusion
were found in RTILs. These extraordinary findings have been
given different explanations, ranging from accelerated diffu-
sion13,14 and ET occurring in the alkyl chain regions of the
RTIL,15 to a tentative statement on too simplified a data
analysis.9,12

The interpretations of the results obtained in RTILs are very
often based on the assumption that the measured rate constant
is simply equal to the diffusion rate constant and should
therefore be inversely proportional to the solvent viscosity,
which is indeed very high for RTILs. However, this view of a
fluorescence quenching process is much too simplistic and only
valid at very low quencher concentrations and in nonviscous
solvents. In fact, as illustrated in Figure 1, in a diffusion-
controlled bimolecular quenching process, the quenching rate,
k, is not constant but decreases continuously over time from a
value k0, which is the intrinsic, diffusion-free, ET rate constant,
until it reaches a constant value corresponding to the diffusion-
controlled rate constant, kdiff,19−26 In a first approximation, that
is, assuming spherical reactants of identical radius and contact
quenching distance, r0, kdiff is given by

\[ k_{\text{diff}} = 4\pi n_0 D N A = \frac{8 \cdot 10^6 \pi R T}{3 \eta} \]  

Received: September 1, 2011
Published: January 27, 2012

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dx.doi.org/10.1021/ja208265x | J. Am. Chem. Soc. 2012, 134, 3729−3736
Figure 1. Illustration of the three quenching regimes in a low and high viscosity solvent. The shading represents the time-dependent probability of finding a fluorophore in the S1 state after optical excitation at time zero in the absence of quencher in the solution.

where $D$ is the mutual diffusion coefficient and $\eta$ is the viscosity in cP.

The time dependence of the rate is due to the existence of three distinct quenching regimes: (1) Directly after optical excitation of the fluorophores, the quenching is static and takes place between the reactant pairs that are already at optimal distance. In this case, no diffusion is necessary and thus the quenching rate is the intrinsic ET rate, $k_0$, which remains constant during this process (blue lines in Figure 1). (2) Once these pairs have reacted, quenching occurs between reactant pairs that are further and further apart and which have time to undergo some diffusion. In other words, a hole created by the reaction in the pair distribution distance between fluorophore and quencher molecules gradually increases (see Figure S2 in the Supporting Information). This continues as long as there is no equilibrium between the rate at which the intrinsic reaction occurs and the rate at which the pairs approach each other sufficiently to react. This is the so-called non-stationary or transient regime, during which the reaction rate constantly decreases with time (red lines in Figure 1). (3) Eventually, the remaining reactants are so far apart that quenching is only possible after substantial diffusion and an equilibrium between this diffusional formation of the reactant pairs and their decay on the excited-state lifetime of the fluorophore amounts to a few nanoseconds, as it is usually the case, the stationary regime is never established. One can also see that not only the duration but also the amplitude of the nonstationary regime, that is, the difference between $k_0$ and $k_{\text{diff}}$ (green lines in Figure 1).

EXPERIMENTAL SECTION

3-Cyanoperylene (CNPe) was synthesized according to the literature and purified by column chromatography. N,N-dimethylaniline (DMA) was obtained from Fluka (puriss p.a., 99.5%), distilled under reduced pressure, and stored under argon.

Glycerol (GLY, Alfa Aesar, ultrapure, HPLC grade) was stored water-free under argon and used as received. Dimethylsulfoxide (DMSO) was obtained in binary solvent mixtures of dimethylsulfoxide (DMSO) and glycerol (GLY) with viscosities identical to those of the RTILs. DMSO/GLY mixtures have already been used to study the influence of viscosity on photoinduced ET and other bimolecular reactions. These mixtures have the advantage that, at least macroscopically, many physical quantities, such as dielectric constant, refractive index, or density, remain unchanged over a wide range of molar fractions and thus viscosity.

Additionally, femtosecond time-resolved measurements by fluorescence up-conversion were performed in one RTIL and one DMSO/GLY mixture to investigate the static and transient quenching regimes. Control measurements were performed in a low viscous organic polar solvent, acetonitrile.

We will show that (i) the diffusive motion of the reactants is very similar in RTILs and conventional solvents of comparable viscosity, (ii) the intrinsic ET reaction is solvent controlled, that is, slower than in conventional low viscous solvents, (iii) the previously observed accelerated reaction rates are indeed artifacts of an oversimplified data treatment as suggested by Li et al., and (iv) the ET quenching of CNPe in viscous solvents takes place mostly in the static and transient regimes and should thus be analyzed with a model that can properly account for these regimes, like, for example, differential encounter theory (DET).

a. Chemicals. 3-Cyanoperylene (CNPe) was synthesized according to the literature, and purified by column chromatography. N,N-dimethylaniline (DMA) was obtained from Fluka (puriss p.a., 99.5%), distilled under reduced pressure, and stored under argon.

Glycerol (GLY, Alfa Aesar, ultrapure, HPLC grade) was stored water-free under argon and used as received. Dimethylsulfoxide

different viscosities (Chart 1) using steady-state and subnano-second time-resolved fluorescence spectroscopy, that is, time-correlated single photon counting (TCSPC), to construct Stern–Volmer plots. The results were compared to those obtained in binary solvent mixtures of dimethylsulfoxide (DMSO) and glycerol (GLY) with viscosities identical to those of the RTILs. DMSO/GLY mixtures have already been used to study the influence of viscosity on photoinduced ET and other bimolecular reactions. These mixtures have the advantage that, at least macroscopically, many physical quantities, such as dielectric constant, refractive index, or density, remain unchanged over a wide range of molar fractions and thus viscosity.
(DMSO, Fisher Scientific, U.K., 99.7%) was purified by performing two freezing cycles, in which the remaining liquid portion of about 10% was separated from the frozen DMSO. Acetonitrile (ACN, Roth, ≥99.9%) was stored over a molecular sieve (Aldrich, 3 Å) and under argon.

The room temperature ionic liquids (RTILs), 1-ethyl-3-methylimidazolium dicyanamide (EMIDCA, >98%), 1-butyl-3-methylimidazolium dicyanamide (BMDCA, >98%), and 1-ethyl-3-methylimidazolium ethylsulfate (EMIES, >99%), were purchased from IoLTec (Germany) and heated at 80–100 °C under reduced pressure (2 mbar) for 3 h before use. The water content of the RTILs was determined by Karl Fischer titration (EMIDCA < 200 ppm, BMDCA < 300 ppm, EMIES < 800 ppm).

b. Characterization of the Solutions. The viscosities of the DMSO/GLY mixtures and the RTILs were measured using an Ubbelhode viscosimeter (SI Analytics GmbH, Germany, type IIC), taking the mean of three individual measurements. Both solvent and viscosimeter were allowed to reach the measurement temperature of 20 ± 0.1 °C over a period of 30 min.

CNPe solutions were prepared at least one day before carrying out the experiments to ensure complete dissolution of the fluorophore. All samples were handled under argon throughout the entire preparation and experimental procedure.

For the entire set of experiments, emission from the RTILs was negligible at the used settings. The DMSO/GLY mixtures and ACN did not show any emission. Neither sample degradation nor changes of spectral shape and position were observed upon increasing the quencher concentration in all types of solvents. Thus both exciplex and ground-state complex formation can be excluded.

c. Steady-State Measurements. Absorption spectra were recorded on a Cary 50 spectrophotometer, whereas fluorescence spectra were measured on a Cary Eclipse fluorimeter (step size: 2 nm, excitation slit: 5 nm, emission slit: 2.5 nm). Both experiments were performed using septum sealed 10 mm quartz cuvettes. A more detailed description of the polarization dependent data recording and data treatment can be found in the Supporting Information. In essence, the polarization dependence of the detection system in any fluorimeter can make a proper control of the excitation and emission polarization necessary to obtain correct quenching results.

d. Time-Resolved Fluorescence. Subnanosecond time-resolved fluorescence decays were measured using the time-correlated single photon counting (TCSPC) technique with a setup similar to that described in ref 38. Briefly, excitation at a repetition rate of 10 MHz was performed using a laser diode (Picoquant model LHD-D-C-470) at 470 nm with a pulse duration of 60 ps. The full width at half-maximum (FWHM) of the instrument response function was about 200 ps. Linearily polarized excitation was ensured by passing the excitation beam through a Glan-Taylor polarizer. The emission was collected at magic angle after passing through an interference filter of 9 nm bandwidth at a central wavelength of 520 nm. The absorbance of the sample solution was kept below 0.5 at the excitation wavelength in a 10 mm septum sealed cuvette.

Femtosecond time-resolved fluorescence decays were monitored using a fluorescence up-conversion setup as described in ref 39. Excitation was performed at 440 nm (Mai-Tai, Spectra Physics) with a repetition rate of 80 MHz. For the emission, 520 and 525 nm wavelengths were chosen for RTIL and DMSO/GLY, respectively, the effective bandpass being 25 nm. At these wavelengths, the contribution of vibrational cooling and/or dynamic solvent shift was minimal and allowed an almost unperturbed observation of the excited CNPe population decay. Nonetheless, the time-decays in the presence of quencher were corrected for the slightly nonexponential intrinsic fluorophore decay before comparison with the model. The FWHM of the instrument response function was 250 fs as determined from the rising edge of the pure CNPe signal. The CNPe concentration was adjusted to obtain an absorbance of less than 0.3 at the excitation wavelength on an optical path length of 0.45 mm in a rotating cell.

Figure 2. Pure fluorescence quenching kinetics (corrected for the intrinsic natural fluorophore decay) measured by TCSPC upon excitation of CNPe at 470 nm in the presence of 0.047 M DMA in acetonitrile (top panel) EMIDCA and a mixture of DMSO/GLY of 17 cP (bottom panel). The red and green lines are exponential decays using the slowest component of a multexponential fit, τlong, to the experimental data (red) and the stationary rate constant, obtained from DET (see text below and Supporting Information), (k_{diff})^{-1}, respectively.

RESULTS AND DISCUSSION

a. ET Quenching and Simple Stern–Volmer Analysis. The fluorescence decay of CNPe in all solvents investigated is strongly accelerated upon addition of DMA, examples being shown in Figure 2. In this figure, the experimentally measured time profiles, I(t,c), have been divided by that recorded without DMA, I(t,c=0), to better appreciate the effect of the quencher.40 The mechanism underlying the quenching of CNPe by DMA is an electron transfer from the amine to CNPe in the S1 state, as confirmed by femtosecond transient absorption spectra recorded after excitation of CNPe at 400 nm. They clearly show the concomitant decay of CNPe in the S1 state and the formation of the CNPe− radical anion (see Figure S5 in the Supporting Information). The radical cation of DMA absorbs comparatively too weakly to be observed. This result also agrees with the calculated driving force for ET, which is larger than 0.3 eV in all the solvents used here.

The fluorescence quenching kinetics in ACN is exponential (Figure 2), while those recorded in the RTILs and in the DMSO/GLY mixtures require the sum of several exponential functions to be satisfactorily reproduced. If we assume that the slowest decay component with a lifetime τ_{long} corresponds to the stationary regime, the following Stern–Volmer equation can be formulated:

\[ \frac{\tau_{f}}{\tau_{long}(c)} = 1 + K_{SV}^c = 1 + k_{q}^c \tau_{ff} \]

where \( K_{SV}^c \) is the Stern–Volmer constant and \( k_{q}^c \) is the experimental quenching rate constant, which, in the stationary regime, should be equal to the diffusion rate constant, \( k_{diff}^c \). The superscript “c” denotes that these values have been determined...
from the decay times. The $k_q^s$ values were obtained from the slope of the Stern–Volmer plots of $\tau_s/\tau_{long}$ versus DMA concentration as shown in Figure 3. They are listed in Table 1 together with the $k_{diff}$ values estimated using eq 1.

The quenching rate constant can also be extracted by considering the decrease of the steady-state fluorescence intensity, $I_{ss}$, upon addition of quencher:

$$I_{ss}(c = 0) = I_{ss}(c) = 1 + k_q^s c = 1 + k_{diff}^s c + k_q^s c$$

(3)

where the superscript "s" specifies that these values originate from a so-called steady-state Stern–Volmer plot. These plots, performed for the CNPe fluorescence quenched by DMA in ACN, RTILs, and DMSO/GLY mixtures, are shown in Figures 3 and 4. Although eq 3 predicts a linear dependence of the fluorescence intensity ratio on the quencher concentration, a strongly nonlinear behavior is observed in all solvents. At constant viscosity, the curvature of the Stern–Volmer plot is even larger in the DMSO/GLY mixture than in the RTIL. This deviation from linearity is a direct manifestation of the static and transient quenching regimes that will be discussed in more detail below. In fact, a similar result would be obtained from the “time-resolved” Stern–Volmer analysis, eq 2, using the average decay time instead of $\tau_{long}$. As the contribution of both static and transient regime increases with quencher concentration, the Stern–Volmer constant, $K_{SV}$, and $k_q^s$ depend on the quencher concentration. This effect is well-known and, to avoid it, eq 3 is usually used at low quencher concentrations only, where the dependence is mostly linear.

The quenching rate constants, $k_q^s$, obtained using eq 3 at low quencher concentrations are also listed in Table 1. In ACN, $k_q^s$ is essentially equal to $k_q^s$ and to $k_{diff}^s$, indicating that the contribution of static and transient quenching regimes is negligible when using eq 3 in the low concentration limit. On the other hand, in the RTILs, the discrepancy between $k_q^s$ and $k_{diff}^s$ is even larger than that already found with $k_q^s$. Indeed, the $k_q^s/k_{diff}^s$ ratio increases from 4.2 to 20 when going from the least to the most viscous RTIL. Here again, this effect is not intrinsic to the RTILs, as it is also present in the DMSO/GLY mixtures, where the $k_q^s/k_{diff}^s$ ratio changes from 5 to 26.

Both time-resolved and steady-state Stern–Volmer plots reveal that the quenching is more efficient in the DMSO/GLY mixtures than in the RTILs of the same viscosity. This points to the RTILs, as it is also present in the DMSO/GLY mixtures, where the ratio increases from 2.6 to 5.6.
toward a slower ET in the latter solvents. The observed difference increases with the quencher concentration and the solvent viscosity. This finding is substantiated by the early quenching dynamics measured by fluorescence up-conversion in EMIDCA and DMSO/GLY of 17 cP after excitation with femtosecond laser pulses (Figure 5). Clearly, the early stage of the reaction is faster in the solvent mixture than in the RTIL. However, after about 10 ps, both fluorescence profiles exhibit an almost parallel decay. This can also be seen in the nanosecond quenching profiles (Figure 2) and points toward very similar diffusion coefficients in both types of liquids. This apparent similarity of translational diffusion coefficients is further supported by identical femtosecond time-resolved fluorescence anisotropy decays of CNPe in ACN (Figure S4 in the Supporting Information), pointing to very similar reorientational dynamics in both types of solvents.

In summary, we find from the above model-free data analysis that the ET quenching in RTILs is not faster than in polar organic solvent mixtures of similar viscosities. Moreover, apart from ACN, the quenching rate constants deduced for a simple Stern–Volmer analysis of the fluorescence quenching are much larger than the diffusion rate constants. A similar result has already been reported in RTILs and has been ascribed to some specific property of these solvents. However, our measurements reveal that the same effect takes place in conventional dipolar solvents of similar viscosity. Thus, the ionic nature of the solvent cannot be invoked to account for this phenomenon.


The above results indicate that a Stern–Volmer analysis using eqs 2 and/or 3 cannot properly account for the quenching of CNPe fluorescence in viscous solvents. Indeed, these equations are only valid in the stationary regime where $k_q$ is constant. Because of this, either the initial part of the quenching dynamics or the quenching data measured at high concentrations, where both the static and transient stages of the quenching are dominating, have to be omitted. As shown in Figure 1, the more viscous the solution, the longer the duration and amplitude of the transient regime where the quenching rate changes from the intrinsic ET rate, $k_{q}$, to the diffusion rate constant, $k_{d}$.

A crude estimate of the lower limit for the duration of the transient regime is given by the encounter time, $\tau_e = r_0^2/D$, where $r_0$ is the quenching radius. This time is approximately the duration of an encounter of the two reactants where they experience the same solvent fluctuations. The fluorescence decay in ACN as shown in Figure 2 indicates that the stationary regime is being approached within the time-resolution of the experiment, which is of the order of 200 ps. This is in good agreement with an encounter time of about 150 ps, calculated assuming contact quenching ($r_e = r_0$). On the other hand, the encounter times calculated for solvents of 17, 36, and 129 cP amount to 1, 2, and 7 ns, respectively. Comparing these values with the fluorescence lifetime of CNPe by DMA in the RTILs and the DMSO/GLY mixtures.

A full account of the quenching dynamics requires the application of a model allowing the analysis of all three quenching regimes. We will use here the so-called differential encounter theory,43 that, contrary to the more popular Collins–Kimball model,44 allows for any distance dependence of the ET process. In DET, the time profile of the fluorescence intensity is given by:

$$I(t) = I(0) \exp\left(-\frac{t}{\tau_f} - c \int_0^t k(t') \, dt'\right)$$

(4)

where $k(t)$ is no longer a constant and is thus called quenching rate coefficient. The latter can be expressed as

$$k(t) = 4\pi \int_{r=r_0}^{\infty} w(r) n(r, t) r^2 \, dr$$

(5)

where $w(r)$ is the reaction probability that depends on the inter-reactant distance, $r$, and $n(r, t)$ is the reactant pair distribution function (see the Supporting Information for further details). The time dependence of this distribution function is at the origin of the transient effect. During the static and transient stages of the quenching, the pair distribution at short $r$ decreases continuously until the equilibrium between the disappearance of the pairs by quenching and their formation by diffusion is established. From then on, the pair distribution function is independent of time and the stationary quenching regime is reached. When determining $n(r, t)$, one should consider that the solvent–solvent pair distribution function of molecular liquids is not flat at short distances due to the excluded volume effect.42 As a consequence, it is more likely to find reactant pairs in close contact than at slightly larger distances. Eventually, at large interparticle distances, this effect disappears and gives rise to a homogeneous distribution function. This effect, which basically translates into an increased effective concentration of close pairs compared to the bulk concentration,42 enhances the reaction rate in the static regime and has to be taken into account. Moreover, the diffusion between reactants is not homogeneous either, due to the hydrodynamic hindering of the mutual diffusion. In simple words, whenever two reactant molecules approach each other, they feel a drift force directed in the opposite direction, which decreases the mutual diffusion coefficient at short distances. The detail of the determination of the reactant pair distribution taking into account these latter two effects is discussed in the Supporting Information.

The reaction probability, $w(r)$, was modeled using Marcus ET theory (eq. S9 in the Supporting Information).43 Because of the high viscosity of the solvents used here, their finite dielectric response time, $\tau_D$, was included in the preexponential factor.44–47 For ACN, this value has been taken from the literature,48 whereas for the RTILs, this quantity has been adjusted. Finally, for DMSO/GLY, a constant value that has
Table 2. Input and Best-Fit Parameters Obtained from the Analysis of the Time-Resolved Fluorescence and Steady-State Stern–Volmer Plot Using eq 4

<table>
<thead>
<tr>
<th>Parameter</th>
<th>ACN</th>
<th>EMIDCA</th>
<th>BMIDCA</th>
<th>EMIES</th>
<th>DMSO/GLY 17 cP</th>
<th>DMSO/GLY 36 cP</th>
<th>DMSO/GLY 129 cP</th>
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</thead>
<tbody>
<tr>
<td>$r_0$, Å</td>
<td>6.6</td>
<td>7.0 ± 0.1</td>
<td>7.0 ± 0.1</td>
<td>7.0 ± 0.1</td>
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<tr>
<td>$V_0$, meV</td>
<td>31</td>
<td>28 ± 1</td>
<td>28 ± 1</td>
<td>28 ± 1</td>
<td>29 ± 1</td>
<td>29 ± 1</td>
<td>29 ± 1</td>
</tr>
<tr>
<td>$\beta$, Å⁻¹</td>
<td>1.08</td>
<td>1.14 ± 0.03</td>
<td>1.14 ± 0.03</td>
<td>1.14 ± 0.03</td>
<td>1.11 ± 0.03</td>
<td>1.11 ± 0.03</td>
<td>1.11 ± 0.03</td>
</tr>
<tr>
<td>$\Delta G$, eV</td>
<td>−0.53</td>
<td>−0.31</td>
<td>−0.33</td>
<td>−0.53</td>
<td>−0.56</td>
<td>−0.56</td>
<td>−0.56</td>
</tr>
<tr>
<td>$r_0$, ps</td>
<td>0.3</td>
<td>4</td>
<td>8</td>
<td>28</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>$\lambda_\text{e}$, eV</td>
<td>0.86</td>
<td>0.72</td>
<td>0.73</td>
<td>0.88</td>
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<tr>
<td>$D$, Å² ns⁻¹</td>
<td>350</td>
<td>7.3</td>
<td>3.3</td>
<td>1.0</td>
<td>7.3</td>
<td>3.3</td>
<td>1.0</td>
</tr>
<tr>
<td>$k_0$, 10⁻¹ M⁻¹ s⁻¹</td>
<td>580</td>
<td>80</td>
<td>40</td>
<td>15</td>
<td>380 ± 40</td>
<td>380 ± 40</td>
<td>380 ± 40</td>
</tr>
</tbody>
</table>

$^a$r₀: contact radius; $V_0$: coupling matrix element at $r_0$; $\beta$: attenuation constant; $\Delta G$: driving force at $r_0$ calculated using Supporting Information eq (S14); $r_0$: longitudinal dielectric relaxation time; $\lambda_\text{e}$: reorganization energy at $r_0$; $D$: mutual diffusion coefficient at infinite reactant separation; $k_0$: intrinsic ET rate constant.

The dielectric constants of the RTILs, especially those of EMIDCA and BMIDCA, are smaller than those of the DMSO/GLY mixtures (Chart 1). Because of this, the driving force, $−\Delta G$, decreases in the two less viscous solvents by more than 0.2 eV.

Table 2 reveals that the intrinsic ET rate constant, that is, the quenching rate constant in the static regime, $k_0$, is substantially slower in the RTILs than in the DMSO/GLY mixtures. Such a faster static quenching in the dipolar solvents was already anticipated from the larger curvature of the steady-state Stern–Volmer plots (Figure 3) and the faster early fluorescence dynamics (Figure 5). After this static stage, quenching is dominated by diffusional effects and thus proceeds similarly in RTILs and the DMSO/GLY mixtures of the same viscosity.

The larger intrinsic ET rate constant in DMSO/GLY can have various origins:

1. The dielectric constants of the RTILs, especially those of EMIDCA and BMIDCA, are smaller than those of the DMSO/GLY mixtures (Chart 1). Because of this, the driving force, $−\Delta G$, decreases in the two less viscous solvents by more than 0.2 eV.

2. The dielectric solvent relaxation times in the RTILs are substantially larger than those of the DMSO/GLY mixtures. Given the moderate driving force of ET between CNP and DMA, the stabilization of the ionic product by solvation is crucial and thus the solvent response may become a controlling factor as already observed in many photoinduced charge separation processes in various solvents, including RTILs.

Despite the apparent success of this Marcus-based analysis of the data, one should bear in mind that there are current concerns about its applicability in quantitative terms. The main issue for dispute is based on the use of the continuum dielectric approximation for the description of RTILs. Despite this, previous work by Lynden-Bell suggests its applicability to be granted even for RTILs. In any case, this model gives a very successful explanation of the observed changes in the ET rate constant.
consistent rationale of the quenching of CNPe by DMA in all solvents investigated.

It is now possible to explain quantitatively the strong discrepancy found between the quenching rate constants obtained from simple Stern–Volmer analysis, that is, $k_q$ and $k_{0,t}$, and the diffusion rate constant, $k_{\text{diff}}$. Figure 6 shows the time dependence of the quenching rate coefficient, $k(t)$, calculated with the best-fit parameters obtained in the three RTILs and in the DMSO/GLY mixtures. In the most viscous RTIL, this constant amounts to $k_0 = 1.5 \times 10^{10} \text{ M}^{-1} \text{s}^{-1}$ at early times and decreases continuously over time to reach a constant value of $k_{\text{diff}} = 5 \times 10^7 \text{ M}^{-1} \text{s}^{-1}$. This represents a decrease of the quenching rate by a factor of about 300! However, this variation is relatively slow. As a consequence, only a small part of this change is accessible in a fluorescence quenching experiment, because of the finite lifetime of the excited-state population. Therefore, the slowest decay component of the fluorescence measured in the TCSPC experiment reflects the quenching rate coefficient at a given time depending on the lifetime of the fluorophore but not the stationary value $k_{\text{diff}}$ that is attained only after more than a microsecond. This time window shrinks with decreasing fluorescence lifetime. Thus, upon addition of quencher, the effective quenching rate coefficient increases continuously toward $k_0$. This explains why the quenching rate constant $k_q$ is much larger than $k_{\text{diff}}$ and why this difference increases with viscosity.

This relatively slow variation of $k(t)$ has an even more dramatic effect when performing a steady-state Stern–Volmer plot. In this experiment, the measured intensity does not depend on the value of $k$ at a given time but reflects a kind of time-averaged value of $k_t$ starting at time zero, where $k = k_0$, to a time $t$ depending on the lifetime of the fluorophore, where $k > k_{\text{diff}}$. As the excited-state lifetime decreases with increasing quencher concentration, this averaging is done over a continuously shorter time window and the measured value tends toward $k_0$. Therefore, the quenching rate constant $k_q$ is even larger than $k_{\text{diff}}$.

**CONCLUSIONS**

The above results show that, at least in the cases studied here, photoinduced bimolecular electron transfer reactions in RTILs are not faster than in conventional solvents but behave as expected for diffusion-controlled processes. In the particular case of electron transfer, the dielectric relaxation of the solvent plays a major role in the control of the reaction rate, and the intrinsic ET rates found here are even faster in conventional polar solvents than in RTILs. However, our experiments do not exclude the existence of specific effects that could, in some special circumstances, result in a faster diffusion.

The difficulty when studying bimolecular quenching processes in RTILs arises from their high viscosity. Because of this, the establishment of the stationary diffusional quenching regime can take several tens of nanoseconds or longer, and as conventional organic fluorophores have an excited-state lifetime of about 10 ns, quenching occurs almost entirely in the static and transient regimes. This results in strongly nonlinear steady-state Stern–Volmer plots—that even at low quencher concentrations—cannot be analyzed with the Stern–Volmer equation. Doing this yields quenching rate constants that are much larger than the stationary rate constant and that depend strongly on the excited-state lifetime of the fluorophore.

As a consequence, there are only two options to obtain reliable rate constants for photoinduced bimolecular reactions in RTILs: (1) use a chromophore with a sufficiently long excited-state lifetime, like a molecule in the triplet state, so that most of the quenching occurs in the stationary regime, with the advantage that the shortening of the long decay component, $\tau_{\text{long}}$, in a time-resolved experiment, or the decrease of the steady state intensity, $I_\infty$, at low quencher concentration, can be analyzed with the Stern–Volmer equation; or (2) use an ordinary fluorophore with an excited-state lifetime of the order of a few nanoseconds with the consequence that reliable information can only be obtained from the analysis of the fluorescence time profile with a theoretical model accounting for all three quenching regimes, like, for example, DET applied here. The inconvenience of this latter approach lies in the fact that it requires a model for the reaction rate, like the Marcus model used here. However, our study shows that this approach allows for a coherent description of one and the same reaction in solvents of very different viscosity and nature, without the need to invoke any additional extraordinary effects for only a few solvents.

**ASSOCIATED CONTENT**

Supporting Information
Femtosecond time-resolved anisotropy decays. Details on data treatment and the theoretical model. Transient absorption spectra in EMIDCA. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was supported by the Fonds National Suisse de la Recherche Scientifique through the NCCR MUST and the University of Geneva.

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