

The influence of molecular oxygen on transient absorption and transient photocurrent kinetics

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Abstract

The transient absorption and transient photocurrent kinetics of photoinduced intermolecular electron transfer reactions in solution can show considerable discrepancies at different molecular oxygen concentrations. The lifetimes of the radical anions observed by transient absorption are decreased in the presence of oxygen, and this is explained by a secondary charge shift reaction of the primary radical anion to oxygen, generating the oxygen anion. Transient photocurrent kinetics are only slightly affected, because no net charge loss results from this mechanism and only the mobility of the corresponding charge carriers changes. © 1997 Elsevier Science S.A.

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1. Introduction

In studies of photoinduced intermolecular electron transfer (ET) reactions in solution, the presence of free ions can be demonstrated by the measurement of the transient photocurrent (TP) [1] after laser flash excitation. For reversible systems, the decay kinetics of the photocurrent should follow those of the optical absorption spectrum of the radical anion or radical cation, since second-order recombination of the ionic transients re-forms the ground state species through diffusional encounter [2]. It is therefore disturbing to find considerable discrepancies between the kinetics of TP and transient absorption (TA) in some cases, as shown in this paper. However, it will be shown that this can be readily explained by the influence of dissolved molecular oxygen (O_2). It is well known that the presence of O_2 causes a variety of undesirable effects in many analytical techniques, e.g. electrochemical analysis, high-performance liquid chromatography and luminescence measurements [3]. In photoinduced reactions, O_2 plays several roles, depending on the spin state of the excited molecule and the excited state energy. Diffusion-controlled collisional energy transfer generating singlet O_2 ($^1O_2^*$) and spin-allowed catalysed intersystem crossing deactivate the excited state [4]. Moreover, O_2 not only interferes with the excited state, but can also play an important role in secondary reactions following the photoinduced ET

processes. Anions formed by photoinduced ET reactions undergo charge shift (CS) reactions with O_2 generating O_2^- [5,6].

2. Experimental details

The TA and TP set-ups have been described elsewhere [1]. The photocurrent cell allows degassing to be performed by the freeze-pump-thaw-shake (FPTS) technique. The ion yields (Φ_{ion}) of the ET reactions were obtained by comparison of the TP peak currents of the argon-bubbled samples with the system benzophenone-diazabicyclo[2.2.2]octane (BP-DABCO) in acetonitrile (MeCN) [1] as reference. The donor concentrations were sufficiently high to ensure that quenching of triplet BP was over 95% efficient. The excitation source for the fluorescence lifetime measurements was a subnanosecond PRA N_2 laser (model LN100) operated at a repetition rate of 10 Hz (337 nm, 300 ps pulse length, 40 μ J energy per pulse). Using a conventional monochromator/photomultiplier set-up, the signal was displayed through an anodic load of 50 Ω onto a 100 MHz digital oscilloscope (Gould, model 4074) and transferred to a computer for further data processing. Deoxygenation of the samples was performed either by the FPTS method or by bubbling argon through the solutions (through a needle with a diameter of 0.8 mm), the flow rate being measured with an "MeTeRaTe" flowmeter tube (Glass Precision Engineering Ltd.). All measurements were performed in MeCN (Fluka, UV grade).

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3. Results and discussion

3.1. Control of the O₂ concentration

Since O₂ can have many different effects on photoinduced reactions, deoxygenation of the samples is very important. Many deoxygenation procedures have been mentioned in the literature, such as vacuum, purge and chemical methods [3]. The most popular technique is inert gas purging without application of a vacuum. It simply involves bubbling nitrogen or argon through the sample, but its efficiency depends strongly on the gas flow and is in any case rather limited. The observation of the pyrene fluorescence lifetime enables the efficiency of the deoxygenation methods to be compared (Table 1).

3.2. Transient photocurrent vs. transient absorption

In the well-documented photoinduced ET reaction between BP and DABCO in MeCN [2,7], the excited triplet BP takes an electron from ground state DABCO and yields quantitatively ($\Phi_{\text{ion}} = 1$ [8,9]) the solvated ions BP^{•-} and DABCO^{•+}. Fig. 1 shows the TA decay kinetics at 710 nm (the absorbing region of BP^{•-} [10]) obtained by different deoxygenation methods. Clearly the lifetime of BP^{•-} is shorter when O₂ is present. Kinetic analysis of the BP^{•-} decay traces demonstrates that only in the best degassed samples (Fig. 1(c)) can the expected second-order disappearance of BP^{•-} be observed. The other traces show first-order (pseudo-first-order) behaviour (Fig. 1(b)) or mixed kinetics. The photocurrent traces (Fig. 2) of differently deox-

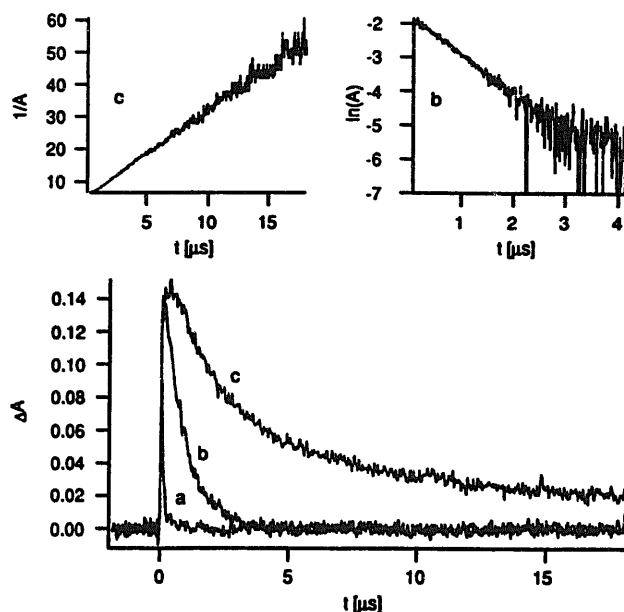


Fig. 1. TA decay kinetics of BP^{•-} observed at 710 nm: (a) not degassed; (b) bubbled for 10 min by a medium argon flow; (c) three FPTS cycles. The insets show the second-order recombination kinetics for (c), but pseudo-first-order recombination kinetics for (b).

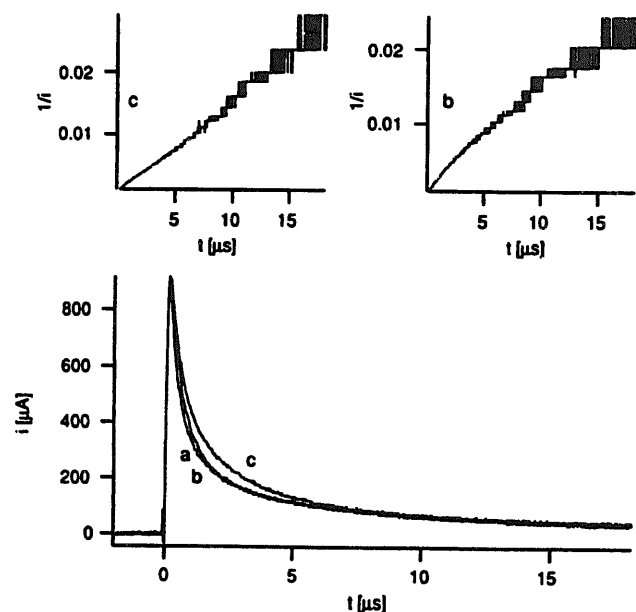


Fig. 2. TP decay kinetics of BP-DABCO in MeCN: (a) not degassed; (b) bubbled for 10 min by a medium argon flow; (c) three FPTS cycles. True second-order recombination kinetics are only observable for (c); (b) $k_{\text{rec}} = 7.8 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$; (c) $k_{\text{rec}} = 9.7 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$.

xygenated BP-DABCO-MeCN samples reveal slight differences. Second-order recombination kinetics are observed only for the FPTS degassed sample (Fig. 2(c)). The others follow second-order kinetics only after a short time delay (Fig. 2(b)). The fitted recombination rate constant shows a slightly greater value for the FPTS degassed sample; nevertheless, the recombination rate constants remain diffusion controlled.

The change in lifetime of the BP^{•-} absorption signal can be explained by the influence of O₂, which quenches BP^{•-}

Table 1

Comparison of the observed fluorescence lifetimes of pyrene in MeCN as a function of the deoxygenation technique

Deoxygenation method		A_{initial}	A_{final}	τ_{obs} (ns) ^a
Argon bubbling				
Gas flow (ml min ⁻¹)	Bubbling time (min)			
15 ^b	0/5/10	0.95	0.95	20/20/20
41 ^b	0/1.5/20	0.95	0.95	20/28/49
108 ^b	0/2/20	0.96	0.99	20/125/125
250 ^b	0/1/20	0.96	1.04	20/40/200
250 ^c	0/1/20	0.96	1.03	20/115/205
500 ^c	0/15	0.96	1.07	20/380
FPTS				
Cycles	Pressure (mbar)			
1	2×10^{-5}	0.96	0.96	385
2	2×10^{-5}	0.96	0.95	430
3	8×10^{-6}	0.95	0.95	450

^a Multiple lifetimes correspond to the different bubbling times.

^b Argon not saturated with solvent.

^c Argon saturated with solvent.

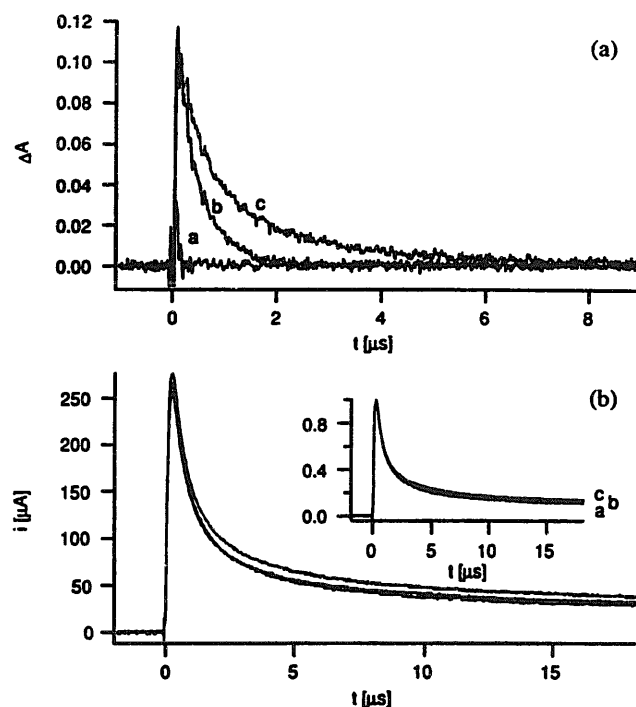


Fig. 3. P-DMA system: (A) TA decay kinetics of $P^{\bullet-}$ at 575 nm; (B) TP decay kinetics, with normalized TP decay kinetics as inset; (a) not degassed; (b) bubbled for 10 min by a medium argon flow; (c) three FPTS cycles.

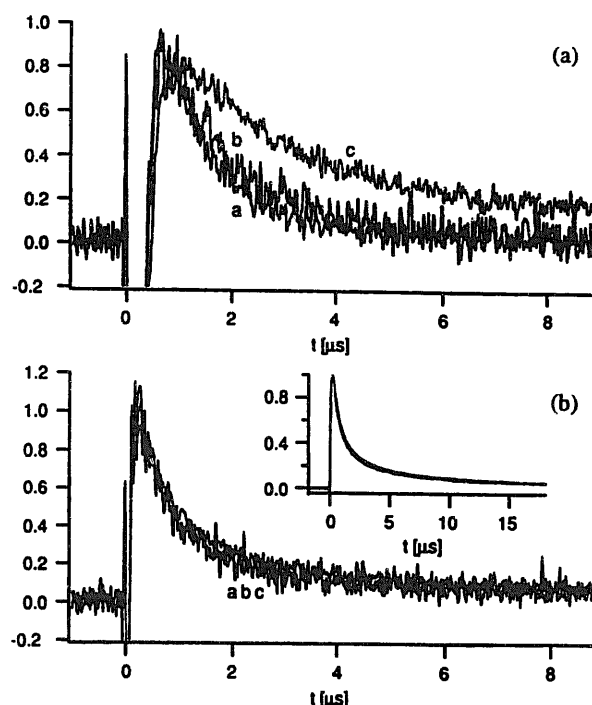


Fig. 4. 9CNP-2MN system: normalized TA decay kinetics of $9CNP^{\bullet-}$ at 430 nm (A) and $2MN^{\bullet+}$ at 580 nm (B); the inset shows the normalized TP decay kinetics; (a) not degassed; (b) bubbled for 10 min by a medium argon flow; (c) three FPTS cycles.

via a CS process and forms $O_2^{\bullet-}$. The fact that only a minor change is observed in the TP signal is due to the slightly different mobility of the new charge carrier which is now $O_2^{\bullet-}$. Due to the very low extinction coefficient ($\epsilon = 650 M^{-1} cm^{-1}$) of $DABCO^{\bullet+}$ at its absorption maximum of 470 nm [11], this transient cannot be observed under our experimental conditions. Another example is the system perylene-*N,N*-dimethylaniline (P-DMA) in MeCN [12]. The TA decay kinetics of $P^{\bullet-}$ at 575 nm in differently degassed samples and the corresponding TP traces are illustrated in Fig. 3.

In order to investigate a system in which the radical cation transient absorption kinetics can also be followed (which should not be affected by such a CS mechanism), several conditions must be fulfilled. The photoinduced ET reaction should have a high ion yield with high extinction coefficients

of the resulting ions. No overall chemical reaction should occur. Both anions and cations should be observable at different wavelengths. In order to obtain an exothermic secondary CS reaction, the reduction potential of the primary acceptor should be lower than that of O_2 . One example is the 9-cyanophenanthrene-2-methoxynaphthalene (9CNP-2MN) ($\Phi_{ion} = 0.53$) couple in MeCN ($\lambda_{obs}(9CNP^{\bullet-}) = 430 nm$, $\lambda_{obs}(2MN^{\bullet+}) = 580 nm$). As expected, only the lifetime of the anion is affected, that of the cation being independent of the oxygen content of the sample (Fig. 4).

The CS reactions described so far are exergonic (Table 2). The choice of a primary acceptor with a reduction potential higher than that of O_2 prevents the CS reaction. Such a case is shown in Fig. 5, which illustrates the pair chloranil (CA)

Table 2

Exergonicity of the secondary CS reaction from the radical anion to oxygen. The lifetime of the radical anion is only affected by oxygen when $\Delta G_{CS} < 0$

Radical anion ($A^{\bullet-}$)	$E_{red}(A)$ (V vs. SCE)	$\Delta G_{CS} (E_{red}(A) - E_{red}(O_2))^a$	O_2 effect on $A^{\bullet-}$
BP $^{\bullet-}$	-1.88 ^b	-1.1	Observed
P $^{\bullet-}$	-1.65 ^c	-0.87	Observed
CNP $^{\bullet-}$	-1.88 ^d	-1.1	Observed
Ca $^{\bullet-}$	-0.02 ^e	+0.76	Not observed

^a $E_{red}(O_2) = -0.78$ (V vs. SCE) [13].

^b Ref. [14].

^c Ref. [12].

^d Ref. [13].

^e Ref. [15].

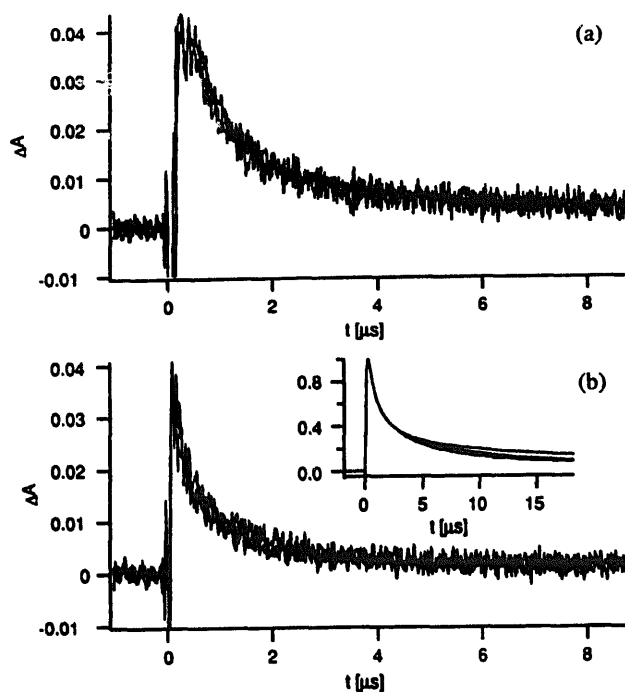


Fig. 5. CA–2MN system: TA decay kinetics of $\text{CA}^{\bullet-}$ at 450 nm (A) and $2\text{MN}^{\bullet+}$ at 580 nm (B); the inset shows the normalized TP decay kinetics; (a) not degassed; (b) bubbled for 10 min by a medium argon flow; (c) three FPTS cycles.

and 2MN ($\Phi_{\text{ion}} = 0.52$). No change in lifetimes, either of the cation or of the anion ($\lambda_{\text{obs}}(\text{CA}^{\bullet-}) = 450 \text{ nm}$ [16]) is observed for differently degassed samples.

4. Conclusions

The TA and TP kinetics of photoinduced intermolecular ET reactions can differ dramatically for different O_2 concentrations. If the reduction potential of the acceptor is lower than that of O_2 , a CS reaction from the radical anion to O_2 generates $\text{O}_2^{\bullet-}$. The lifetime of the primary radical anion is therefore decreased in the presence of O_2 . The TP kinetics are only slightly affected, because no net charge loss results

from such a mechanism, and only the mobility of the corresponding charge carriers changes. In order to avoid erroneous data resulting from the treatment of kinetics obtained by TA, O_2 should be removed from the samples. To obtain satisfactory deoxygenation, the FPTS method is favoured over the conventional bubbling method.

Acknowledgements

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