97. Laserflash-Photolysis of the *p*-Chloranil/Naphthalene System: Characterization of the Naphthalene Radical Cation in a Fluid Medium¹)

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Dedicated to Prof. *E. Giovannini* on the occasion of his seventieth birthday

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Summary

Excitation of *p*-Chloranil (**CA**) in propylcyanide (PrCN) at room temperature leads to rapid production of ^{3}**CA*** which decays predominantly to **CAH**$^{\cdot}$ with $k_d^0 = 1.6 \cdot 10^5\ s^{-1}$. Observation of a photoinduced current suggests simultaneous production of **CA**$^{\dot{-}}$ formed by electron transfer quenching of ^{3}**CA*** by the medium. Added naphthalene (**NP**) quenches ^{3}**CA*** with $k_q = 7.0 \cdot 10^9\ \text{M}^{-1}\ s^{-1}$; **NP**$^{\dot{+}}$ is unambigously identified as product (besides **CA**$^{\dot{-}}$) of the electron transfer process. Dissociation of the ion pair occurs with essentially unit probability. Higher concentrations of **NP** lead to the formation of $(\mathbf{NP})_2^{\dot{+}}$. Pertinent spectroscopic parameters established for **NP**$^{\dot{+}}$ under the conditions used are $\lambda_{max} = 685$ nm ($\varepsilon = 2970$) using the known parameters of **CA**$^{\dot{-}}$ as reference. **NP**$^{\dot{+}}$ and **CA**$^{\dot{-}}$ decay by charge annihilation with $k_r = 4.5 \cdot 10^9\ \text{M}^{-1}\ s^{-1}$. The deviation from the diffusion controlled rate constant expected for ionic species, is discussed in view of the spin characteristics of the process. Comparison with two other ion recombination reactions leads to the conclusion that 'inverted behaviour' as expected from *Marcus'* theory does also not show up for *backward* e^--transfer between two ions (produced by forward e^--transfer between two neutrals). Residual absorptions in the system are ascribed to **CAH**$^{\cdot}$, tentatively proposed to originate from H^+-abstraction by **CA**$^{\dot{-}}$ from the solvent. **NP**$^{\dot{+}}$ appears to be a rather stable species with respect to the medium if the latter is meticulously purified.

Introduction. - Various methods are available for the production of the radical cations **M**$^{\dot{+}}$ of organic molecules **M** in condensed media [2]. In the case of hydrocarbons, many aromatic examples could be detected in fluid media; others, however, required the use of solid matrices because of their low kinetic stability. The forerunner among this latter highly reactive class is provided by **M**$^{\dot{+}}$ = 2,2,3,3-tetramethylbutane$^{\dot{+}}$, observed by *Symons* after γ-irradiation of parent **M** at 77 K [3]. Aromatic radical cations larger than naphthalene$^{\dot{+}}$ (**NP**$^{\dot{+}}$) were identified under

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¹) Part V of 'Studies on Radical Cations'; part III & IV: [1].

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fluid conditions. **NP**$^{+}$ itself, however, escaped unambiguous spectroscopic characterization and its occurrence was postulated by indirect reasoning. Thus, **NP**$^{+}$ must have been involved in various photoinduced electron transfer reactions as the corresponding acceptor radical anions could be identified [4] [5], a transient photocurrent was observed [6] or the kinetic features of the process fitted the *Weller* scheme [7]. Furthermore, pulse radiolysis of **NP** in various solvents produced a transient species which was assigned to **NP**$^{+}$ on the basis of its electronic spectrum [8] [9] [10]. While some (but not all) of the bands reported in [8] find their parallel in the reference spectrum of genuine matrix-isolated **NP**$^{+}$ [11], the corresponding conclusions drawn in [9] and [10] are rather optimistic[3]. That **NP**$^{+}$ must be a very reactive short-lived species is also supported by electrochemical work, where little, if any, clear-cut mechanistic information is available for its reactions with nucleophiles [13]. Indeed, even the true thermodynamic oxidation potential of **NP** is still uncertain as shown by the irreversibility of the electrode process, suggesting rapid destruction of **NP**$^{+}$ after its formation. (The reported values for $E^{\mathrm{ox}}_{1/2}$ (NP/NP^{+}) have increased over the years, peaking now at 1.84 V (*vs.* SCE) obtained by means of *Parker*'s technique [14].) Finally, chemical or electrochemical attempts to prepare salts of **NP**$^{+}$ in inert media result exclusively in the formation of the dimer cation salts $(\mathrm{NP})_2^{+}\ \mathrm{X}^{-}$ [15].

The above cited observations initiated the present work, which reports on **NP**$^{+}$ prepared by the electron transfer quenching of the triplet of *p*-chloranil (^{3}**CA***) by **NP** in propylcyanide (PrCN) at room temperature (22°):

$$^3\mathbf{CA}^* + \mathbf{NP} \rightarrow \mathbf{CA}^{-} + \mathbf{NP}^{+} \qquad (1)$$

Results and Discussion. - 1. *Concerning the choice of the e$^-$-acceptor* ^{3}**CA***. *Figure 1* shows some energy levels of the present system with respect to ground state **NP** + **CA**. The free energy change of electron transfer (ΔG_{et}) in forming the ion pair from ^{3}**CA*** and **NP** in the quenching act is given [17] by:

$$\begin{aligned}\Delta G_{\mathrm{et}} &= E^{\mathrm{ox}}_{1/2}(\mathrm{NP/NP^{+}}) - E^{\mathrm{red}}_{1/2}(\mathrm{CA^{-}/CA}) - \Delta E_{00}(^3\mathrm{CA}^*) - \mathrm{C} \qquad (2)\\ &\hat{=}\ 1.84\ \mathrm{eV}\ [14] - 0.02\ \mathrm{eV}\ [18] - 2.13\ \mathrm{eV}\ [16] - 0.1\ \mathrm{eV}\\ &= -0.41\ \mathrm{eV}.\end{aligned}$$

The *Coulomb* term $\mathrm{C} = \mathrm{e}^2/\mathrm{r} \cdot \varepsilon$ amounts to 0.1 eV for the ion pair in PrCN ($\varepsilon = 20.3$), assuming r = 700 pm as the encounter distance [17]. The oxidation and reduction potentials were measured in MeCN (*vs.* SCE); solvation energy changes in passing from MeCN to PrCN are assumed to cancel in (2). The use of ^{3}**CA*** as acceptor thus ensures thermodynamic feasibility of the electron transfer step and also of the dissociation of the complex into free solvated ions (see *Fig. 1*). On the other hand triplet energy transfer yielding ^{3}**NP*** is excluded. Detection of the free ions is favoured by the fact that **CA**$^{-}$ absorbs at shorter wavelengths ($\lambda_{\mathrm{max}} = 450$ nm [19]) than **NP**$^{+}$ ($\lambda_{\mathrm{max}} = 700$ nm [11]). Finally, the photophysics and photochemistry of **CA**

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[3] Donorsubstituted NP^{+}-ions could be spectroscopically identified both in condensed [7] and in the gas phase [12].

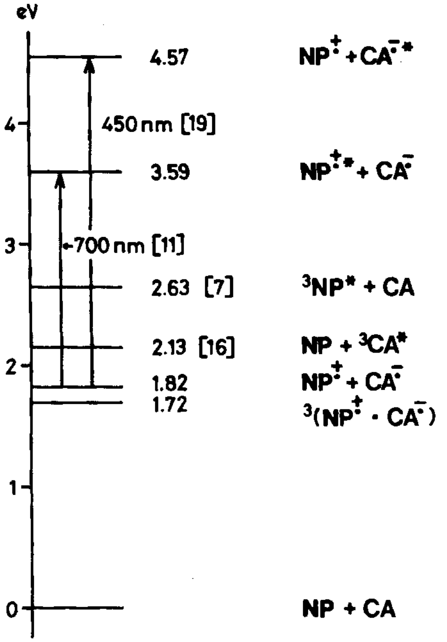


Fig. 1. *Energy levels of pertinent systems*

are reasonably well established [20–28]. The choice of PrCN as solvent will be justified below.

2. *Photolysis of* CA *in PrCN.* Excitation of CA in PrCN by the frequency-tripled Nd-laserpulse (353 nm) results in the immediate formation of a transient species absorbing at 510, 480 and 380 nm *(Fig. 2),* which on the basis of earlier work is ascribed to $^3CA^*$ [20–27]. Incident flash energy and observed absorption are linearly related; hence $^3CA^*$ is produced in a monophotonic process. $^3CA^*$ exhibits a first

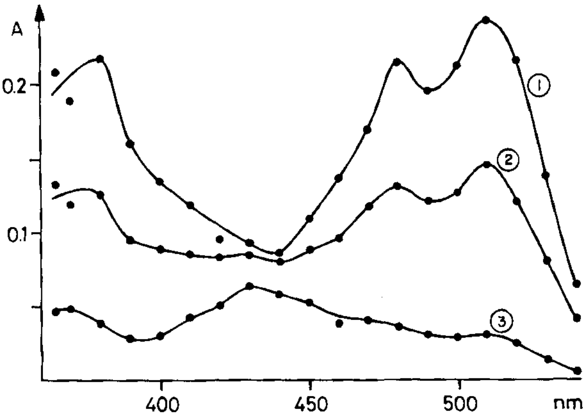


Fig. 2. *Photolysis of* CA *in PrCN, observed transient spectra.* Delay times are (after flash): ①, immediately; ②, 1 μs; ③, 4 μs

order decay which is significantly enhanced by adding oxygen. The decay constant in PrCN is $k_{\mathrm{d}}^{0} = 1.6 \cdot 10^{5}\ \mathrm{s}^{-1}$, in good agreement with earlier measurements in other solvents, *i.e.* $1.8 \cdot 10^{5}\ \mathrm{s}^{-1}$ in dichloroethane [27], $8.4 \cdot 10^{5}\ \mathrm{s}^{-1}$ in ethanol [21] and $5 \cdot 10^{5}\ \mathrm{s}^{-1}$ in cyclohexane [21].

After decay of $^{3}\mathbf{CA}^{*}$ a longer lived transient species is noted with absorption maxima at 430 nm and 370 nm, decaying with a second order rate law. These absorptions have also been observed earlier in MeCN [23] [27] and ascribed to the semiquinone radical $\mathbf{CAH}^{\cdot}$. We feel confident that the same assignment also applies in the present case, particularly as we established that $\mathbf{CA}^{\overline{\cdot}}$ in PrCN absorbs at 450 nm *(vide infra)*. However, there have been speculations about the simultaneous production of the latter anion from $^{3}\mathbf{CA}^{*}$ in MeCN [27]. (We note in this context that the decay of $^{3}\mathbf{CA}^{*}$ in alcohols yields exclusively $\mathbf{CA}^{\overline{\cdot}}$ [26].) This question cannot be resolved purely on spectral grounds as $\mathbf{CAH}^{\cdot}$ and $\mathbf{CA}^{\overline{\cdot}}$ have rather similar absorption spectra in the $\lambda > 400$ nm region. To shed further light on this problem we followed the decay of $^{3}\mathbf{CA}^{*}$ by simultaneously measuring the photoconductivity of the solution, using MeCN and PrCN as solvents and for both experiments the same conditions (A at 353 nm = 0.305, applied voltage U = 500 V). In both cases a photocurrent i_{rel} was observed with maximum intensity for $t \sim 2$ µs after the flash ($t = 0$), indicating the production of charge carriers (among them most probably $\mathbf{CA}^{\overline{\cdot}}$) during the decay of $^{3}\mathbf{CA}^{*}$. The peak current found for MeCN was five times that of PrCN.

Walden & Birr [29] have shown that the product of molar conductivity Λ_{m}^{0} (at infinite dilution), the macroscopic viscosity coefficient η of the medium and the hydrodynamic radius r is approximately constant for a given ion with a given concentration in different solvents:

$$\Lambda_{\mathrm{m}}^{0} \cdot \eta \cdot r = \text{const.} \tag{3}$$

With η (MeCN) = 0.34 cP, η (PrCN) = 0.57 cP [30], $r_{\mathrm{MeCN}} \sim r_{\mathrm{PrCN}}$ we deduce from (3) $[\mathrm{ions}]_{\mathrm{PrCN}}/[\mathrm{ions}]_{\mathrm{MeCN}} \sim 0.3$, *i.e.* PrCN leads to only 30% free ion production compared to MeCN.

These ions most probably evolve from outersphere electron transfer quenching of $^{3}\mathbf{CA}^{*}$ by solvent molecules. Dissociation of the intermediate complex into free solvated ions is favoured by a high dielectric constant ε of the solvent if the complex has a high degree of ionicity. If not, the coordinating properties of the solvent as measured by its donicity (DN) and acceptor (AN) numbers are more decisive, as pointed out by *Gutmann* [31]. PrCN is disfavoured with respect to MeCN for all these three parameters. Hence, regardless of the nature of the initial complex, a lower free ion yield in the case of PrCN is not unexpected.

Absolute yields of ion production are unfortunately not available from our experiments and we can therefore not comment on the relative yields of $\mathbf{CAH}^{\cdot}$ and $\mathbf{CA}^{\overline{\cdot}}$ from $^{3}\mathbf{CA}^{*}$. At any rate, we decided to conduct the following experiments in PrCN in order to minimize the build-up of $\mathbf{CA}^{\overline{\cdot}}$ and of the associated photocurrent from e^{-}-transfer quenching of $^{3}\mathbf{CA}^{*}$ by the medium itself.

Our postulate of $\mathbf{CAH}^{\cdot}$ being formed through H$^{\cdot}$-abstraction from PrCN by $^{3}\mathbf{CA}^{*}$ may contrast at first sight with the puzzling experience that the C–H bonds of MeCN are rather inert towards ketone triplets which on the other hand readily engage in H$^{\cdot}$-abstractions from various substrates [32] with C–H bonds of generally much higher strength (D) [33]. To comment on this:

From [33] one can deduce that for most of the H$^{\cdot}$-donor investigated the rate of H$^{\cdot}$-abstraction by a given triplet roughly increases with decreasing D. The high exothermicity associated with H$^{\cdot}$-abstraction from an H–C(α)-group of an alkyl nitrile, however, may place the transition state rather early on the reaction coordinate and the stabilization experienced by an alkyl radical from a CN-group [34] may therefore not come into play. This argument alone, however, is insufficient to rationalize the lack of reactivity, given that D of the C–H bonds vicinal to benzene have about the same strength but are readily cleaved by the triplets [33]. We suggest that the inertness of the C(α)–H bond of nitriles is related to the electrophilic nature of the triplets as there is considerable positive charge placed on the protons vicinal to the CN-group. These arguments obviously do not apply to PrCN as here more remote though stronger bonded H$^{\cdot}$-atoms are available for abstraction. To check on these *contra Bell-Evans-Polanyi* arguments we photolyzed benzophenone (**BP**) in MeCN and PrCN. The decay of ^{3}**BP*** in MeCN was strictly second order indicating a decay of the state *via* T–T annihilation. A plot of ln[^{3}**BP***] *vs.* t for PrCN showed, however, after an initial slight curvature (T–T annihilation?) strict linearity, indicating a pseudo first order kinetics. The (approximated) rate constant log$k$ = 6 deduced from this part of the curve compares well with the results obtained for pure hydrocarbon H$^{\cdot}$-donors [33]. The results thus support the above arguments. They further place some doubts on the conclusion delivered in [27] that CAH$^{\cdot}$ is formed directly from ^{3}CA* also in MeCN. We note that this conclusion derives from the kinetical analysis of the 420 nm absorption of CAH$^{\cdot}$, which, however, is strongly shared by CA$^{\overline{\cdot}}$ (shoulder at 420 nm, *Fig. 3* and [19]).

3. *Photolysis of* CA *in PrCN in the presence of* NP. - 3.1. *Quenching of* ^{3}CA* *by* NP; *production of* CA$^{\overline{\cdot}}$ *and* NP^{+}. In the presence of excess NP the decay of ^{3}CA* *(Fig. 3)* follows a first order rate law, the decay constant k_{d} obeying

$$k_{\mathrm{d}} = k_{\mathrm{d}}^{0} + k_{\mathrm{q}} \cdot [\mathrm{NP}] \tag{4}$$

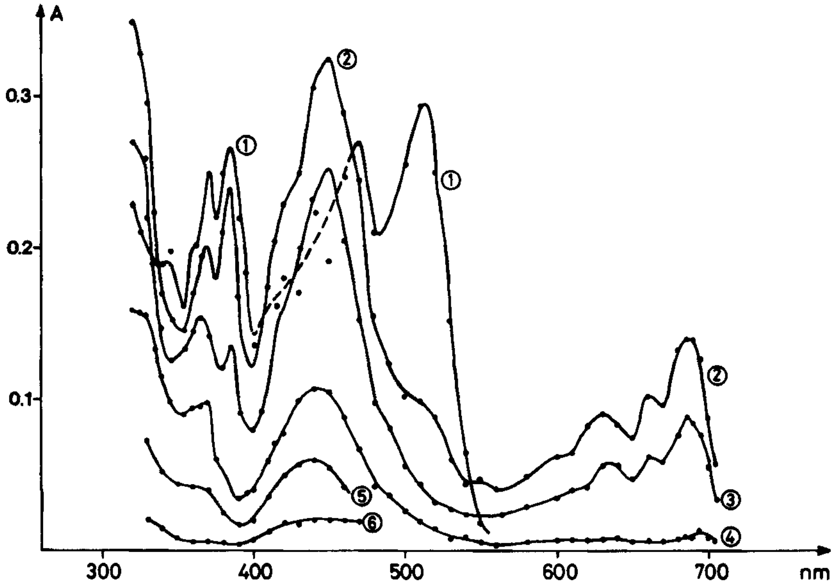


Fig. 3. *Quenching of* CA *in the presence of* NP *in PrCN, observed transient spectra.* [NP] = 1.73 · 10^{-3}M, [CA] = 0.81 · 10^{-3}M, d = 2 cm. Delay times are (after flash): ①, immediately; ②, 300 ns; ③, 1.2 µs; ④, 5 µs; ⑤, 20 µs; ⑥, 100 µs

Table 1 gives values for k_d and the quenching constant k_q as a function of [**NP**] (see also oscilloscope trace in *Fig. 4*). The quenching is accompanied by the rise of two band systems *(Fig. 3)*. The one at 450/420 nm (sh) is perfectly compatible with the spectrum reported for the sodium salt of $\mathbf{CA}^{\overline{\cdot}}$ in MeCN [19]. The long wavelength band system with $\lambda_{max} = 685$ nm and the clearly discernible vibrational progression at higher energy ***establishes unambiguously*** the presence of $\mathbf{NP}^{\overline{\cdot}}$ (compare [11]).

The products above thus suggest that a *Weller*-type quenching-scheme [35] prevails:

$$\begin{tikzcd}
 & & {} \\
\mathbf{CA} + \mathbf{NP} \arrow[r, "h\nu"] & {}^1\mathbf{CA}^* + \mathbf{NP} \arrow[r, "\Phi_T"'] & {}^3\mathbf{CA}^* + \mathbf{NP} \arrow[u, "k_d^0"'] \arrow[d, "k_q"] \\
\mathbf{CA}^{\overline{\cdot}} + \mathbf{NP}^{+\cdot} \arrow[u, "k_r", "\Phi_r"'] & & (\mathbf{CA}^{\overline{\cdot}} \cdots \mathbf{NP}^{+\cdot}) \arrow[ll, "k_{sep}\text{, }\Phi_{sep}"']
\end{tikzcd} \qquad (5)$$

That the observed quenching constant is also compatible with this scheme is shown as follows: From *Marcus*'s theory [36], the rate constant k_{obs} for an activated electrontransfer process ($\Delta G^{\ddagger}_{et}$ = free activation energy) near the diffusion controlled limit (k_{diff}) is given by

$$k_{obs}^{-1} = k_q^{-1} = k_{diff}^{-1} + 10^{-11} \exp(\Delta G^{\ddagger}_{et}/RT). \qquad (6)$$

Assuming the hydrodynamic radii of the two components to be equal, the modified *Debye* relation [37] holds

$$k_{diff} = 8\ RT/3\ \eta \qquad (7)$$

which yields, with $\eta = 0.57$ cP and $T = 295$ K, $k_{diff} = 1.15 \cdot 10^{10} \mathrm{M}^{-1} \mathrm{s}^{-1}$. The empirical relation (8) for $\Delta G^{\ddagger}_{et}$ was shown to be valid for a wide range of positive and negative ΔG_{et} values [35]:

$$\Delta G^{\ddagger}_{et} = \Delta G_{et}/2 + [(\Delta G_{et}/2)^2 + (\Delta G^{\ddagger}_{et}(0))^2]^{1/2}. \qquad (8)$$

$\Delta G^{\ddagger}_{et}(0)$ represents the free activation energy for an electron transfer process with $\Delta G_{et} = 0$; a value of 10 kJ mol^{-1} has been derived for this quantity in MeCN [35]. As it is known to depend only slightly on the solvent and the system involved [36], we adopted it also for PrCN. With $\Delta G_{et} = -0.41$ eV *(Fig. 1)* we thus obtain from (6), (7) and (8) $k_q = 8.8 \cdot 10^9 \mathrm{M}^{-1} \mathrm{s}^{-1}$, in good agreement with the experimental value $k_q = 7 \cdot 10^9 \mathrm{M}^{-1} \mathrm{s}^{-1}$. Note that the calculated value may in fact be slightly too large as $\Delta G_{et} = -0.41$ eV is based on an oxidation potential for **NP** which is still irreversible [14], the true thermodynamic one being therefore somewhat higher.

The above analysis was performed on the basis of signals attributed to the free ions. The agreement with the theoretical prediction indeed supports the idea that the

Table 1. *Quenching of* $^3\mathbf{CA}^*$ *by* **NP** *in PrCN, pseudo first order decay constants and calculated quenching constant* ([CA] = $1.7 \cdot 10^{-3}$M)

[NP] $\cdot 10^3$	[M]	0	0.84	1.3	4.6	5.0	7.3	12.8	
$k_d \cdot 10^{-6}$	[s^{-1}]	0.16 (= k_d^0)	5.3	9.1	36	36	50	100	
$k_q \cdot 10^{-9}$	[M^{-1} s^{-1}]		5.7	6.6	7.7	7.2	6.8	7.8	mean 7.0

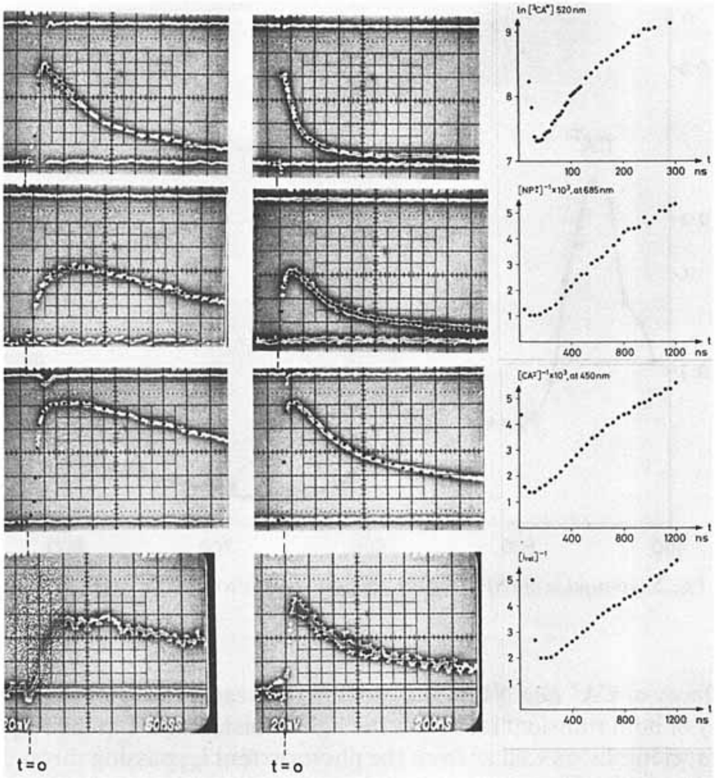


Fig. 4. *Oscilloscope traces at two different time scales* (left) *and graphical analysis* (right) *for the time dependent absorptions of* $^3CA^*$, NP^+ *and* $CA^{\bar{\cdot}}$, *and the time dependent photocurrent of the ions* (see text)

rate of ion formation is exclusively determined by the quenching step and not by the separation of the ion-pair (rate constant k_{sep} in (5)). We note, however, that the spectrum of the ion-pair may well involve transitions localized within the components and situated at energies not too different from those of the separated individuals [38]. To shed light on this question we applied *Eigen*'s diffusion controlled ion-pair dissociation model [39] to our solvent PrCN, using for the solvent independent parameters those given in [40]. We found $k_{\text{sep}} = 1.1 \cdot 10^9\ s^{-1}$, a value which requires that free ion formation ought to be instantaneous on our time scale which is determined by the duration of the laser pulse ($\tau_{1/2} \sim 20$ ns). Experimental verification of this prediction stems from the observation that the photoinduced peak-current appears without delay with respect to the peak absorption of the ions *(Fig. 4)*.

Finally, we note that for high concentrations of **NP** (0.7 M) a different transient spectrum appears immediately after the flash *(Fig. 5)*. The signals are easily assigned to $\mathbf{CA}^{\bar{\cdot}}$ and the dimer cation radical $(\mathbf{NP})_2^{\dot{+}}$ exhibiting characteristic bands at 1050 and 580 nm [41]. Apparently, initially produced $\mathbf{NP}^{\dot{+}}$ is scavenged by **NP** in a process near diffusion control [41] whose time scale (for the concentrations needed) is beyond that of our apparatus.

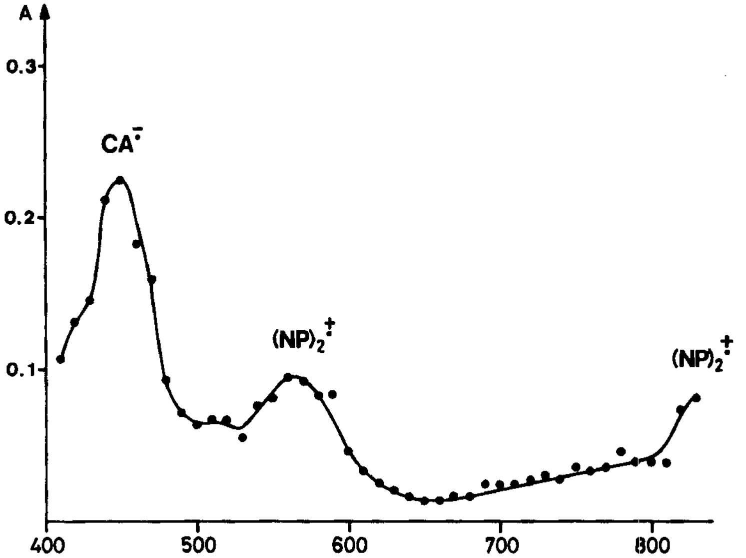


Fig. 5. *Absorption of* $(NP)_2^{+}$ *in PrCN immediately after flash* (see text). ([NP] = 0.7 M)

3.2. *Decay of* CA^{-} *and* NP^{+}. The oscilloscope traces in *Figure 4* show the build-up and decay of both transient ions from the light transmission T at the respective characteristic wavelengths, as well as from the photocurrent i_{rel} passing through the solution. A plot of $(\log T)^{-1}$ (taken in the early decay region) *vs.* t yields for both ions a reasonably straight line, indicating that they decay by a second order recombination (rate constant k_r in (5)). As the same result is obtained from plotting i_{rel}^{-1} *vs.* t, the above recombination involves charge exchange. (The deviation from linearity for later stages of the decay will be discussed in a subsequent chapter.)

To obtain k_r we embarked on a numerical analysis of the combined build-up and decay kinetics of the consecutive pseudo-uni/bimolecular reaction (5), based on oscilloscope traces for both NP^{+} and CA^{-} such as shown in *Figure 4*. The solution of the differential equations has been given by *Chien* [42]. The reader is referred to his work and to [43]; additional information specific to the present problem is found in the experimental part.

The above treatment requires concentration data as input and therefore a knowledge of certain extinction coefficients (in $M^{-1}cm^{-1}$), either ε_{510} ($^3CA^*$) alone or both ε_{685} (NP^{+}) and ε_{450} (CA^{-}). This problem was handled as follows: interception of >99% $^3CA^*$ by NP (*i.e.* $\Phi_q > 0.99$) requires k_q [NP] > 100 k_d^0, or with the data given in *Table 1* [NP] > $2.3 \cdot 10^{-3}$ M. Two solutions (①, ②) of CA ($1.7 \cdot 10^{-3}$ M, PrCN), one of them (②) containing also NP ($6 \cdot 10^{-3}$ M) were photolyzed under identical conditions and the peak absorptions due to $^3CA^*$ at 510 nm (from ①), CA^{-} at 450 nm (from ②) and NP^{+} at 685 nm (from ②) recorded. The ratio between these must be equal to the ratio of the corresponding extinction coefficients as the concentrations of the ions are the same, and - provided $\Phi_{sep} = 1$ - also equal to the initial concentration of the triplet. Using as reference value $\varepsilon_{\max}(\mathrm{CA}^{\overline{\cdot}}) = 9700$ from the sodium salt in MeCN [19] we arrive at

$$\varepsilon_{510}(^3\mathrm{CA}^*) = 7570 \quad \text{and} \quad \varepsilon_{685}(\mathrm{NP}^+) = 2970. \tag{9}$$

Some points in support of these values shall be discussed before proceeding:

(i) A value $\varepsilon_{\max}(^3\mathrm{CA}^*) = 7200$ has been determined in dichloroethane [27], in good agreement with our result;

(ii) The quantum yield for ^{3}CA*-formation can be obtained using the method of *Amand & Bensasson* [44]:

$$\Phi_\mathrm{T}(^3\mathrm{CA}^*) = \Phi_\mathrm{T}(^3\mathrm{X}^*) \cdot \frac{\varepsilon(^3\mathrm{X}^*) \cdot \mathrm{A}(^3\mathrm{X}^*)}{\varepsilon(^3\mathrm{CA}^*) \cdot \mathrm{A}(^3\mathrm{CA}^*)} \tag{10}$$

from the ratio of concentrations (prop. $\varepsilon \cdot \mathrm{A}$; A = absorbance) of instantaneously formed ^{3}**CA*** and of a triplet ^{3}**X*** with known quantum yield of formation. Both triplets are prepared under identical instrumental conditions and, in particular, using solutions of reactands exhibiting the same absorbance at the exciting wavelength. We chose **X** = benzophenone in benzene with $\Phi_\mathrm{T} = 1$ and $\varepsilon_{532.5} = 7630$ from [45], which led to $\Phi_\mathrm{T}(^3\mathrm{CA}^*) = 0.98 \pm 0.05$. This result is in accord with what one expects for **CA** in view of the fact that already less halogenated quinones possess $\Phi_\mathrm{T} \sim 1$ [20-22] [27]. It in turn supports our value for $\varepsilon_{510}(^3\mathrm{CA}^*)$;

(iii) *Kira et al.* [46] gave $\varepsilon_{\max} = 6800$ for the 700 nm band system of **NP**$^+$ obtained by γ-irradiation in a low temperature freon matrix. Assuming the total oscillator strength of the transition to be independent of the medium, comparison between the spectrum used by them (from [11]) and the one recorded by us *(Fig. 3)* by the weighting method yields $\varepsilon_{685}(\mathrm{NP}^+) = 3200$, in good agreement with (9).

We conclude that the values given in (9) are sufficiently reliable to be used in the simulation of the kinetics of the observed process. In addition the agreements allow us to conclude that Φ_sep is essentially unity, *i.e.* that practically all ion pairs dissociate into free ions and none decay directly to ground state neutrals. In principle, this latter step is unfavorable as a considerable amount of potential energy (1.72 eV) would have to be converted into heat, resulting in small *Franck-Condon* factors for the transition. Nevertheless, $\Phi_\mathrm{sep} \ll 1$ has been found in several singlet systems [47]. We, therefore, are inclined to attribute our findings to the fact that for the present triplet system decay to ground state neutrals is not observed because it would require a multiplicity change.

Using the above mentioned input values together with oscilloscope traces such as shown in *Figure 4* yields the following solutions of the *Chien*-equations (for calculatory details see experimental part):

$$\begin{aligned} k_\mathrm{q} &= (6.5 \pm 0.5) \cdot 10^9\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}, \\ k_\mathrm{r} &= (4.5 \pm 0.5) \cdot 10^9\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}. \end{aligned} \tag{11}$$

While k_q in (11) as obtained from the complete analysis of the ions' dynamics is in excellent agreement with the earlier value found by considering the decay of ^{3}**CA*** alone, the value for k_r provides some surprise, as it is significantly smaller than diffusion controlled.

The rate of diffusion of two ions of unit charge ($k^{\mathrm{i}}_{\mathrm{diff}}$) is approximately related to that of two neutrals through

$$k^{\mathrm{i}}_{\mathrm{diff}} = 0.8 \cdot k_{\mathrm{diff}} \cdot \mathrm{P}, \tag{12}$$

where

$$\begin{aligned} k_{\mathrm{diff}}(\mathrm{MeCN}, 295\ \mathrm{K}) &= 1.8 \cdot 10^{10}\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}, \\ k_{\mathrm{diff}}(\mathrm{PrCN}, 295\ \mathrm{K}) &= 1.15 \cdot 10^{10}\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}, \end{aligned} \tag{13}$$

and

$$\mathrm{P} = \frac{\mathrm{a} \cdot \mathrm{b}}{{}_{\mathrm{e}}\mathrm{a} \cdot \mathrm{b}_{-1}}; \quad \mathrm{a} = (\mathrm{R} \cdot \varepsilon)^{-1}; \quad \mathrm{b} = \frac{\mathrm{e}^2}{4\pi\,\varepsilon_0\,\mathrm{kT}}. \tag{14}$$

R is the distance at which reaction occurs (taken to be equal for ions and neutrals in the derivation of (12)), ε the dielectric constant of the medium, and the symbols appearing in b have their usual meaning. The factor of 0.8 in (12) allows for the fact that the diffusion coefficients of solvated ions are around 20% smaller than those of neutrals [48]. P is larger (smaller) than unity for ions of equal (opposite) charge [49]. Assuming R = 700 pm (*i.e.* the distance at which (forward) e$^-$-transfer quenching occurs [17]) yields P = 4.1 for our solvent PrCN. Therefore, the observed ion annihilation rate is only 13% of the expected $k^{\mathrm{i}}_{\mathrm{diff}}$. A similar analysis for two other ion annihilation reactions in MeCN (P = 2.44) reported by *Weller et al.* [48] and by *Levin* [50] results in corresponding percentages of 29 and 21%, respectively. Alternatively, assuming an effective encounter distance of R = 1000 pm (~ two solvent layers [51]) yields P = 3.0 for PrCN, P = 1.94 for MeCN and reduced rates corresponding to 16, 36 and 28%, respectively, for the above three systems in the same order. Such reduced rates may in principle be expected on the basis of *Marcus'* theory [52] as the free energies (1.86, 2.41, 1.61 eV) or enthalpies (which are smaller by roughly 0.2 eV = $-\mathrm{T} \cdot \Delta_r S^0$ [51]) to be converted on neutralization into heat are quite considerable and small *Franck-Condon* factors may result. (Note that none of the above enthalpies suffices to produce electronically excited neutrals). If this point would apply, however, vastly different reduction-factors would be expected for *Weller*'s system with respect to ours or *Levin*'s. 'Inverted behaviour' as predicted by *Marcus'* theory has never been observed in (forward) e$^-$-transfer quenchings of purely organic donor/acceptor systems despite extensive searches (see [52]). *It appears that this feature also fails to show up for (backward) e$^-$-transfer on decay of the corresponding anion/cation complex.*

Alternatively, the low rates may indicate a state symmetry forbidden e$^-$-transfer process [53]. Analysis shows, however, that all the ions involved have $^2\Pi$-ground states and that a sandwich-type encounter complex of C_2- and/or C_s-symmetry leads to a perfectly allowed e$^-$-transfer. We suggest that the described findings are best rationalized by considering the spin characteristics of the reactions. After dissociation of the initial ion pair of triplet multiplicity the ions escape their mutual *Coulombic* field in the polar solvents used and recombination of the doublets essentially becomes of 'homogenous' or 'interpair' type [54]. Hence, for the ensuing state of the re-encounter pair of randomized spins, the statistical factors ¼ and ¾ for singlet and triplet, respectively, apply where only the former event opens up a decay channel. The theoretical annihilation rate is therefore only 25% of the predicted $k^{\mathrm{i}}_{\mathrm{diff}}$, in reasonable agreement with the observed retardation if the errors involved in the kinetical analysis as well as the approximate nature of (12) are taken into account.

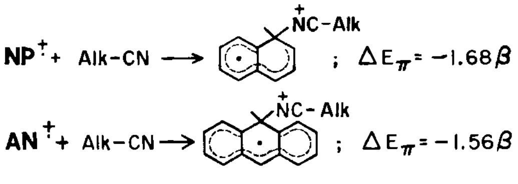
We finally mention that the disappearance of $\mathrm{CA}^{\dot{-}}$ and $(\mathrm{NP})_2^{\dot{+}}$, prepared using high [NP] as discussed earlier, also follows a second order rate law with same rate constant, indicating that they analogously recombine.

3.3. ***Residual absorptions.*** After decay of $\mathrm{CA}^{\dot{-}}$ and $\mathrm{NP}^{\dot{+}}$ a weak absorption at 430 nm remains, decaying with a second order kinetics reminiscent to that found for $\mathrm{CAH}^{\cdot}$ in chapter 2. This and the spectral feature leads us to assign the species to $\mathrm{CAH}^{\cdot}$. Interestingly, the above is observed also for concentrations of NP where essentially all $^3\mathrm{CA}^*$ are scavenged by the hydrocarbon; its formation, then, cannot be ascribed to $\mathrm{H}^{\cdot}$-abstraction from the solvent by the triplet. An alternative route of $\mathrm{CAH}^{\cdot}$ formation must then be followed which we tentatively propose to be H^+-abstraction from the solvent by some fraction of initially formed $\mathrm{CA}^{\dot{-}}$. We note that a carbanion is considerably stabilized by a CN-substituent [34]. Nucleophilic attack of $\mathrm{CA}^{\dot{-}}$ on the positivized C(*a*)-protons of PrCN is thus not inconceivable.

It has been known for some time that the radical anions of certain quinones and aromatic hydrocarbons are able to abstract protons from weak acids [55]. Thus, anthraquinone anion reacts in this manner with benzoic acid in DMF with $k_p \sim 1.5 \cdot 10^4 \mathrm{M}^{-1} \mathrm{s}^{-1}$ [56]. For a rough estimate of the corresponding rate constant in our system we first note from *Figure 3* that $[\mathrm{CAH}^{\cdot}]_{\max} \sim 0.1 [\mathrm{CA}^{\dot{-}}]$, given $\varepsilon_{430}(\mathrm{CAH}^{\cdot}) \sim \varepsilon_{450}(\mathrm{CA}^{\dot{-}})$. A mean value for the life time of $\mathrm{CA}^{\dot{-}}$ with respect to its predominant decay path *via* ion recombination with $\mathrm{NP}^{\dot{+}}$ is ~ 1 µs under the conditions valid for the results of *Figure 4*. Hence, $k_p[\mathrm{PrCN}] \sim 0.1 \cdot 10^6 \mathrm{s}^{-1}$, or, with $[\mathrm{PrCN}] = 11 \mathrm{M}$, $k_p \sim 10^4 \mathrm{M}^{-1} \mathrm{s}^{-1}$. This estimated order of magnitude is not incompatible with the proposed H^+-abstraction mechanism in view of the above cited reference value.

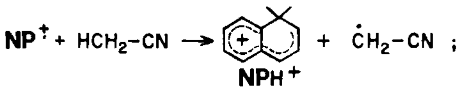
Final Comments. - As mentioned in the introduction photolysis of mixtures of NP and various acceptors A have been investigated in the past. Although the transient absorptions due to $\mathrm{A}^{\dot{-}}$ were identified, the spectrum of the pertinent radical cation $\mathrm{NP}^{\dot{+}}$ was not observed, in contrast to the results reported in this paper. This situation also prevailed in the work of *Levin* [50] who investigated perylene radical cation. Our experience parallels his observations that the respective cations disappear much more rapidly than $\mathrm{A}^{\dot{-}}$ whenever the solvents were not *meticulously* purified, particularly with respect to water. In line with this *Parker* and collaborators were able to show that the use of 'super clean' (or perhaps better 'super-dry') solvents [14] allows one to measure reversible electrode potentials for redox couples which always behaved irreversibly in these solvents when purified by standard techniques.

Alkyl nitriles are, however, intrinsically not as inert towards aromatic radical cations as has generally been presumed [57]. 'Super-clean' MeCN nucleophilically attacks anthracene (AN) radical cation at C(9) and/or C(10), albeit with a rather small (pseudo first order) rate ($k = 125 \mathrm{s}^{-1}$ [58]). $\mathrm{NP}^{\dot{+}}$ is expected to be less reactive given the following changes in HMO π-energies for the hydrocarbon moieties:



(15)

Furthermore, H$^{\cdot}$-abstraction from the nitrile by **NP**$^{\dot{+}}$ is unfavorable on thermochemical grounds (shown for MeCN)[4]):



(16)

$$\Delta H^{\circ} = 74.4\ \mathrm{kJmol^{-1}}$$

We conclude that pure alkyl nitriles should be rather inert towards **NP**$^{\dot{+}}$, in line with our experimental experience. (We note in passing that H$^{\cdot}$-abstraction by benzene$^{\dot{+}}$ could well be a source of its unstability as here $\Delta H^0 = -3.3$ kJ mol^{-1} for the analogous process (16)[4])). The slight deviations from second order behaviour at later stages of the ion recombination reaction shown in *Figure 4* in fact indicate that **NP**$^{\dot{+}}$ may be even more stable than **CA**$^{\dot{-}}$! The deviation for the latter must result from an increasing absorption at 430 nm, *i.e.* from the build-up of **CAH**$^{\cdot}$. It cannot be explained by an additional decay route for **CA**$^{\dot{-}}$ showing up, with products not absorbing at this wavelength, as it simulates an apparent *decreasing* rate constant. The same reason, however, is not available in the case of **NP**$^{\dot{+}}$, as no long-lived residual absorption is found at 685 nm. Apparently, the rate of depletion of **NP**$^{\dot{+}}$ decreases excessively because increasing amounts of the recombination partner **CA**$^{\dot{-}}$ are consumed in the side reaction with the solvent.

In a following paper [61] the electronic spectrum of **NP**$^{\dot{+}}$ obtained here will be compared with the spectra obtained under other conditions, and with the PE. spectrum of **NP**. Solvent effects on the spectrum of this radical cation will be discussed.

Experimental Part. - *Apparatus.* Excitation was provided by a frequency tripled *JK* 2000 Nd-glass laser, the energy of a single pulse at $\lambda = 353$ nm being ~ 100 mJ. The relative energy of successive pulses was monitored by passing the beam through a quartz plate and feeding the reflected portion into a *Molectron* J3-05 Joule meter; variations in energy up to 20% had to be taken into account. Changes of the beam image ('hot spots') at the sample are also a source of unsatisfactory correlations between incident energy and resulting transient absorbance; therefore, mean values obtained from several shots were used in the numerical analysis.

A K-347 detection system of *Applied Photophysics* was employed equipped with an *EMI* 9785 photomultiplier tube providing spectral sensibility up to 830 nm. Concentration gradients in the optical path of the sample were avoided by letting the laser and the monitoring beam enter the 1 cm cuvette at right angles near one corner. Appropriate slits provided an effective volume of 1 × 1 × 2 mm at that corner. The monitoring light source was opened only shortly before flashing in order to minimize photochemical activity in the sample. The signals were recorded with a *Tektronix* 7633 storage oscilloscope.

The transient photoconductivity was measured with the device shown in *Figure 6*, allowing simultaneous observation of the optical changes (see also [62]). Direct illumination of the electrodes was avoided by appropriate optical devices. The focused laser beam entered the sample through the ground

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[4]) The proton affinity PA(NP) = 795.6 kJ mol^{-1} is estimated from PA(benzene) = 767.2 kJ mol^{-1} [59] and $\Delta pK_B = -5.4$ (statistically corrected) for protonation of NA and benzene [60]. The hydrogen affinity HA(NP$^{\dot{+}}$) = 269.9 kJ mol^{-1} results from considering in addition I(NP) = 8.15 eV, EA(H$^+$) = 13.6 eV. With I(benzene) = 9.25 eV, HA(benzene$^{\dot{+}}$) = 347.6 kJ mol^{-1} is obtained. Finally, HA($\dot{C}H_2CN$) = 344.3 kJ mol^{-1} is taken from [34]. Solvation will not greatly influence the outcome for the respective ΔH^0-values as (16) involves neither creation (annihilation) of charges nor charge dispersal effects.

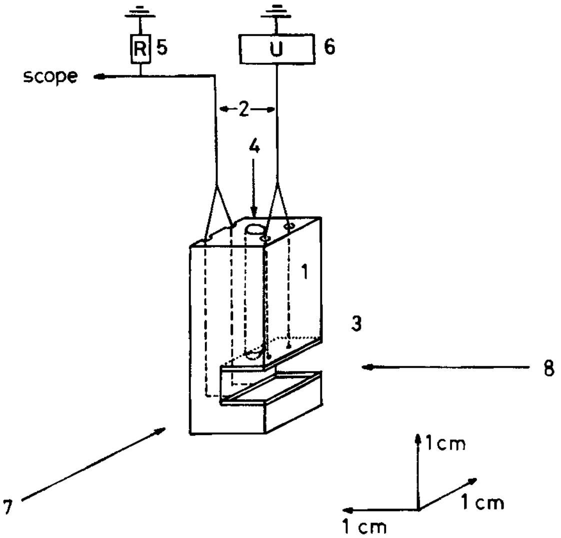

Fig. 6. *Photoconductivity cell, allowing simultaneous recording of absorptions*
1 Teflon block to be placed in 1 cm cuvette; 2 wires; 3 Pt-electrodes; 4 sample inlet; 5 load 50 or 200 Ω; 6 DC-power supply 10-500 V; 7 monitoring light; 8 laser beam.

window whereby light scattering reduced beam inhomogenities. The DC-voltage from a *Brandenburg* 485R power supply could be varied in the range 10-500 V. The current was converted to voltage by a 200 or 50 Ω resistor, the time constant of the circuit being 10 ns for the latter. The signal was fed directly into the preamplifier of the scope through the AC-coupling whereby the dark current could be eliminated (this latter was 2 mA at U = 400 V). The photoinduced peak currents were ~ 1 mA.

Chemicals and sample preparation. CA *(Fluka, puriss.)* was twice recrystallized from benzene, NP (*Roth*, scintillation grade) was sublimed *in vacuo*. PrCN *(Fluka, puriss.)* was purified in analogy to the procedure reported for MeCN [63], then twice fractioned with a spinning band column. After chromatography at activated alumina it was stored over alumina and molecular sieves. The purified solvent is transparent up to ~220 nm ($A_{220} = 0.1$, d = 1 cm). MeCN was purified along the same lines. Benzene was treated with conc. sulfuric acid until the acid layer became colourless. After washing with water and destillation it was dried with and then stored over molecular sieves.

The sample solutions were degassed by freeze-pump-thaw cycles and then purged with dry N_2 in order to prevent bubble formation on laser impact. We were unable to follow *Parker*'s recommendation [14] to conduct all experiments with solutions containing suspended alumina, as CA was adsorbed by it.

Numerical analysis. As the time scales of some rate processes and of the laser pulse are similar, the build-up/decay characteristics of the latter had to be taken into account. The laser intensity as a function of time could be represented by the *Gaussian* [64]:

$$I(t) = N \cdot \exp[-0.0077\,(t-30)^2], \tag{17a}$$

where t is in ns and N is a normalization factor. The origin of time, where I was considered still negligible (I = 0), was set at 30 ns before peak output (t = 30 ns). Accordingly, I = 0 for t > 60 ns was assumed. With

$$Q(t) = f \cdot I(t), \tag{17b}$$

where f was chosen to satisfy

$$\int_{-\infty}^{+\infty} Q(t)\,dt = f \int_{-\infty}^{+\infty} I(t)\,dt = A_0, \tag{18}$$

A_0 = total amount of $^3CA^*$ prepared. The following differential equations describe the dynamics of the system:

$$\dot{A}(t) = Q(t) - k_d A(t) \quad \text{and} \quad \dot{B}(t) = k_d A(t) - k_r B(t)^2. \tag{19}$$

The rate constants are defined in (4) and (5), $A={}^{3}\mathbf{CA}^{*}$, $B=\mathbf{CA}^{\dot{-}}$ or $\mathbf{NP}^{\dot{+}}$, and $A(t=0)=B(t=0)=0$. Note that we assume $[\mathbf{CA}^{\dot{-}}]=[\mathbf{NP}^{\dot{+}}]$ to be a good approximation, *i.e.* we neglect the partial decay of $\mathbf{CA}^{\dot{-}}$ to $\mathbf{CAH}^{\cdot}$ as discussed in 3.3. Furthermore, for all [**NP**] in *Table 1* $k_d \gg k_d^0$ holds; (4) is therefore simplified to $k_d = k_q \cdot \mathbf{NP}$ which is used in (19).

For $Q(t=0)=A_0$ and $Q(t>0)=0$ solutions to (19) were given by *Chien* [42] [43]. For $Q(t)\triangleq(17)$, *i.e.* $0<t\leqslant 60$ ns numerical solution of (19) was achieved by successive linearisation starting from $t=0$:

$$X(t') = X(t) + \Delta t \cdot \dot{X}(t), \tag{20}$$

where $X=A$ or B, $\dot{X}=\dot{A}$ or $\dot{B}$ as taken from (19), and $t'=t+\Delta t$. The program MARFIT (*Marquardt* algorithm) [65] was employed for the curve fitting procedure.

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