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Direct determination of rate constants for coupling between aromatic radical anions and alkyl and benzyl radicals by laser-flash photolysis

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Coupling rates between the radicals methyl, *n*-, *sec*-, *tert*-butyl and benzyl ($R^\bullet$) and the aromatic radical anions of 1,4-dicyanonaphthalene, 9,10-dicyanoanthracene and fluorenone ($A^{-\bullet}$) have been obtained using a new laser-flash photolysis method. The radicals $R^\bullet$ and the radical anions $A^{-\bullet}$ were generated by a photoinduced electron transfer reaction between the aromatic compound A and the alkyl or benzyl triphenylborate anion $RB(Ph)_3^-$. For the first time the rate constants of the coupling reaction between methyl and benzyl radicals with aromatic radical anions have been obtained. For all the measured coupling rate constants an average value of $k_1 = 1.9 \times 10^9$ M^{-1} s^{-1} was found with a relatively small variation in the coupling rates (0.8–2.9 × 10^9 M^{-1} s^{-1}). The results demonstrate that the coupling rate k_1 is insensitive to changes in the steric and electronic properties of the radicals and the structure and standard potentials of the aromatic radical anions.

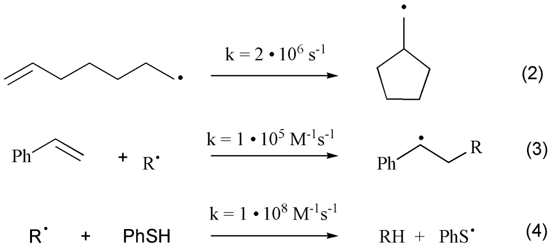
Introduction

Aromatic radical anions are strongly colored species with a versatile and interesting chemistry. They may react both as electron donors,[1–5] bases,[6] nucleophiles[7] and radicals.[8–11] In this paper we will focus on the radical coupling properties of aromatic radical anions. Aromatic radical anions are fairly stable in aprotic media under oxygen-free and dry conditions due to the mutual charge repulsion. They couple, however, very quickly with alkyl and benzyl radicals [eqn. (1)].

$$A^{-\bullet} + R^\bullet \xrightarrow{k_1} AR^- \qquad (1)$$

Knowledge of the coupling rate constant k_1 is important in connection with recent attempts to estimate reversible redox potentials of alkyl and benzyl radicals from measured reduction potentials.[12–15] Several indirect methods have been used to estimate the coupling rate k_1. Thirty years ago, Garst *et al.* obtained the rate constants for the coupling reactions between chemically generated naphthalene and benzophenone radical anions with the 1-hexenyl radical in dimethyl ether and tetrahydrofuran, respectively.[8,9] Later, Pedersen and Lund used the radical clock method to obtain coupling rates between some electrochemical generated radical anions and various radical clocks in dimethylformamide.[10] In some recent work, coupling rates between *tert*-, *sec*- and *n*-butyl radicals with anthracene, *p*-diacetylbenzene and *p*-dicyanobenzene radical anions were obtained by two new indirect methods in which either an activated olefin or thiophenol was added to the solution.[11] The underlying principle of the indirect methods is to establish a competition between the coupling reaction [eqn. (1)] and another reaction with a known rate constant. The competition reactions mentioned above are shown in Scheme 1.

These indirect methods either involve rather tedious product analysis or are restricted to a very limited number of radical anions.[11]



Scheme 1

The conclusion obtained from the indirect rate measurements is that the coupling reaction between alkyl radicals and radical anions is fast with rate constants approaching the diffusion limit, which reflects the lack of significant activation barriers. All measured values were in the range of 0.5–3.5 × 10^9 M^{-1} s^{-1}. This conclusion is based on a relatively small number of measured coupling rates and no information was obtained for coupling rates between benzyl radicals and radical anions. Therefore, in order to further substantiate the previously obtained conclusion and to obtain coupling rate data of the benzyl radical as well, we have developed a new method in which the rate constants of the coupling between radical anions and radicals have been obtained in a direct fashion by means of flash photolysis.

The principle behind the laser-flash method is based upon the photoinduced alkylation chemistry of aromatic compounds by alkyl triphenylborates introduced by Lan and Schuster.[16–18] They showed that irradiation of acetonitrile solutions of dicyanoarenes with methyltriphenylborate or benzyltriphenylborate gave good yields of alkylcyanoarenes. The proposed mechanism is shown in eqns. (5)–(8).

$$A + h\nu \longrightarrow A^* \qquad (5)$$

$$A^* + RB(Ph)_3^- \longrightarrow A^{-\bullet} + RB(Ph)_3\cdot \qquad (6)$$

$$RB(Ph)_3\cdot \longrightarrow R\cdot + B(Ph)_3 \qquad (7)$$

$$A^{-\bullet} + R\cdot \longrightarrow AR^- \qquad (8)$$

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Table 1 Photochemical and electrochemical data of various acceptor compounds A

A	E_0/V *vs.* SCE	$\varepsilon_A(351)^a$	$\lambda_{A^{-\bullet}}$/nm	$\varepsilon_{A^{-\bullet}}{}^a$	τ/ns
1,4-Dicyanonaphthalene	−1.166	506	512	3578	10^c
9,10-Dicyanoanthracene	−1.015	2622	520 640	5440^b 5590^d	15.9^e
Fluorenone	−1.220	162	550	7575^c	

[a] $dm^3\ mol^{-1}\ cm^{-1}$. [b] This work. [c] Ref. 24. [d] Ref. 19. [e] Ref. 31.

The reaction is initiated by a photoinduced electron transfer from the alkyltriphenylborate to the excited acceptor A* followed by a fast cleavage of the alkyltriphenylborane radical (*ca.* 1 ps). The coupling between the radical $A^{-\bullet}$ and R• was shown to take place in the solution.[17] Equal concentrations of $A^{-\bullet}$ and R• are generated after the laser pulse and the second order radical anion radical coupling reaction [eqn. (8)] may be followed by monitoring the absorption change of the aromatic radical anion in the visible part of the spectrum. In order to extract the coupling rate constant k_1 from the second order process between $A^{-\bullet}$ and R• it is necessary to know the extinction coefficient of the aromatic radical anion at the monitoring wavelength. Recently a large number of accurate extinction coefficients of aromatic radical anions have been obtained.[11,19] With these extinction coefficients available, we have been able to obtain the k_1 values of the reactions between the radical anions 1,4-dicyanonaphthalene (DCN), 9,10-dicyanoanthracene (DCA) and fluorenone (FLUO) and methyl, *n*-butyl, *sec*-butyl, *tert*-butyl and benzyl radicals.

Results and discussion

Photoinduced alkylation of aromatic compounds with alkyl and benzyl borates shown in eqns. (5)–(8) is a fairly general process, which is not restricted to cyanoarenes. Recently, the method has been used in preparative photolysis experiments with anthracene and benzophenone as acceptors.[20,21] In the laser-flash experiments described in this work there are, however, some restrictions on the choice of acceptor compounds. A solution of the acceptor without the borate salt should give no absorption at the detection wavelength of the radical anion. With acceptor compounds like anthracene, fluoranthene and perylene non-negligible absorption was observed probably due to two-photon photoionization of the compounds to the corresponding cation radicals $A^{+\bullet}$ and solvated electrons.[22] Furthermore, to obtain reasonable quantum yield of the $A^{-\bullet}$ [eqn. (6)] the lifetime τ of the singlet state A* should not be too short and the borate concentration not too small (>10 mM). The three compounds—1,4-dicyanonaphthalene, 9,10-dicyanoanthracene and fluorenone—fulfill the above requirements. *N*,*N*-dimethylformamide (DMF) was chosen as the solvent due to the high solubility of the borate salts in DMF and because the kinetic data obtained by the laser-flash method could be compared directly with the coupling rates obtained by indirect methods. Key photochemical and electrochemical data of the three compounds are given in Table 1.

Fig. 1 shows a typical radical anion decay trace recorded immediately after the laser pulse. The experiment was performed on an oxygen-free solution of fluorenone (3.11 mM, od = 0.55) and *n*-$BuB(Ph)_3^-$ $N^+(CH_3)_4$ (20 mM) in DMF. The initial absorption was 0.12 and the final absorption after 100 μs was 0.065. If the reaction mechanism shown in eqns. (5)–(8) were complete, the infinite absorption A_{inf} should be zero. However, due to dimerization [eqn. (9)] and disproportionation [eqn. (10)] of $R^\bullet$ there is not enough R• radicals to quench the $A^{-\bullet}$ absorption completely. The shape of the radical anion absorption decay may therefore be explained by the competition between eqn. (1), (9) and (10).

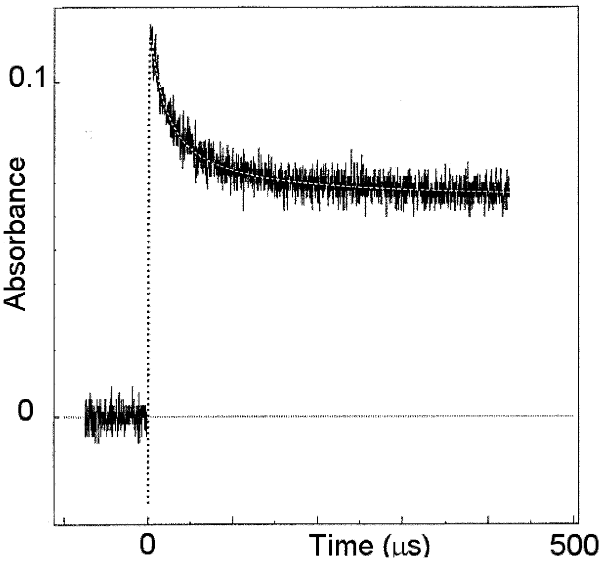


Fig. 1 Laser experiment performed on a solution of fluorenone (3.1 mM) and *n*-$C_4H_9B(Ph)_3^-N^+(CH_3)_4$ (20 mM) in dimethylformamide. The decay of the fluorenone radical anion was monitored at 550 nm. Initial absorbance $A(0) = 0.124$, $A_{inf} = 0.065$ and the apparent second order rate constant $k = 9.4 \times 10^5\ s^{-1}$.

$$A^{-\bullet} + R\bullet \longrightarrow AR^- \qquad (1)$$

$$R\bullet + R\bullet \longrightarrow R\text{–}R \qquad (9)$$

$$R\bullet + R\bullet \longrightarrow RH + R(\text{–}H) \qquad (10)$$

The remaining radical anion concentration of fluorenone shown in Fig. 1 disappeared during the typically 2–3-min time interval between each laser experiment. The same was true for the radical anion of 1,4-dicyanonaphthalene; however, the radical anions of 9,10-dicyanoanthracene are so stable that the radical anion concentration slowly builds up between the laser experiments. After 30 pulses, a nice UV-VIS spectrum identical to the spectrum of electrochemical generated radical anions of 9,10-dicyanoanthracene was obtained with a conventional UV spectrometer.

Reaction mechanism

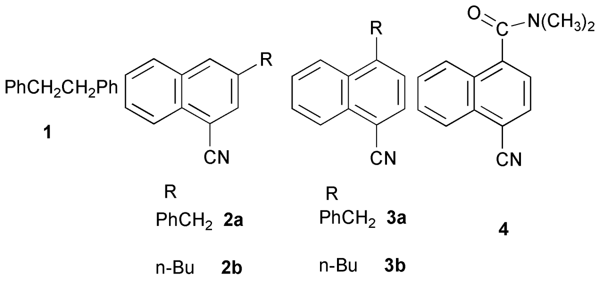
In order to test the proposed decay mechanism, product investigations were performed on laser-pulsed or steady-state irradiated solutions of 1,4-dicyanonaphthalene and benzyl or *n*-butyltriphenylborate in DMF. The identified products are shown in Scheme 2 and the quantum yields of the products RR (**1**), ARH (**2** + **3**) and **4** together with the quantum yield of the disappearance of the acceptor 1,4-dicyanonaphthalene ϕ_{DCN} are shown in Table 2.

The observation of fair yields of the DMF derived product **4** was unexpected (ϕ_4 = 0.02–0.12) and initiated a series of experiments in order to reveal the mechanism of the product formation. Steady-state photolysis of 1,4-dicyanonaphthalene in DMF gave, to our surprise, **4** with $\phi_4 = 0.05$. The mechanism

Table 2 Quantum yields of the products **1**–**4** obtained by preparative photolysis of 1,4-dicyanonaphthalene and $PhCH_2B(Ph)_3^-$, $(CH_3)_4N^+$ in DMF

Exp.	λ_{ex}/nm	Laser pulses/ Irr. time	mol[a] Photons × 10^6	[DCN] mM	R	[Borate] mM	ϕ_{DCN}[b]	ϕ_{RR}	ϕ_4	ϕ_{ARH}[c]
FP1[d]	351	50	2.78	3.89	$PhCH_2$	20	0.31	0.050	0.11	0.12
FP2	351	100	5.56	1.55	$PhCH_2$	24	0.33	0.060	0.12	0.10
FP3	355	300	5.31	1.65	$PhCH_2$	24	0.46	0.012	0.10	0.30
FP4	355	600	10.6	1.65	$PhCH_2$	27	0.32	0.010	0.11	0.36
CW1[e]	321	30 min	15.8	1.86	$PhCH_2$	17	0.27	0.00	0.04	0.24
FP5	355	200	7.8	1.78	*n*-Bu	23	0.23	0.00	0.024	0.16
FP6	355	400	16.6	1.78	*n*-Bu	23	0.20	0.00	0.042	0.12
CW2	321	44 min	1.7	1.78	—	—	0.12	—	0.05	—

[a] Obtained by Aberchrome 540 actinometry.[29] One laser-pulse = 5.56×10^{-8} mol photons. The volume of the photolysis samples was 3.41 ml. [b] Quantum yields of disappearance of 1,4-dicyanonaphthalene. [c] $\phi_{ARH} = \phi_2 + \phi_3$. [d] FP: Laser-flash photolysis. [e] CW: Continuous wave irradiation by tungsten–xenon lamp.



Scheme 2

of this photochemical side reaction may be formulated as a photoinduced electron transfer process [eqn. (11)].

$$DCN^* + 2HC(O)N(CH_3)_2 \longrightarrow [DCN^{-\bullet} + HC(O)N^{+\bullet}(CH_3)_2 + HC(O)N(CH_3)_2] \longrightarrow [DCN^{-\bullet} + HC(O)NH^+(CH_3)_2 + {}^{\bullet}C(O)N(CH_3)_2] \longrightarrow \mathbf{4} + HCN + DMF \qquad (11)$$

The reaction in eqn. (11) is akin to a reaction in a paper by O'Donnel and Mann who studied the direct electrochemical oxidation of aliphatic amides in dimethylformamide.[23] In analogy with their original proposed mechanism, the initially formed cation radical $HCON^{+\bullet}(CH_3)_2$ abstracts a hydrogen atom from a nearby DMF molecule with formation of $HC(O)NH^+(CH_3)_2$ and ${}^{\bullet}C(O)N(CH_3)_2$. Finally $DCN^{-\bullet}$ and ${}^{\bullet}C(O)N(CH_3)_2$ couple with the formation of **4** followed by a loss of HCN. No $DCN^{-\bullet}$ absorption was observed in laser-flash experiments on solutions of DCN dissolved in DMF without a borate salt. Based on this observation it may be concluded that the photochemical coupling process between DCN and DMF does not involve free $DCN^{-\bullet}$ radical anions and the coupling process is likely to occur in the solvent cage. The conclusion of this mechanistic analysis is that even though relative high amounts of **4** are produced in the laser-flash kinetic experiments this does not influence the kinetic decay of the $A^{-\bullet}$. The kinetics of the decay may therefore still be described adequately by eqns. (1), (9) and (10).

Based on the proposed mechanism of the photolysis in DMF eqns. (5)–(11), the following relations may be derived:

$$\phi_{A^{-\bullet}} = \phi_{ARH} + 2\phi_{RR} + (\phi_{RH} + \phi_{R(-H)}) \qquad (12)$$

$$\phi_{DCN} \text{ (of disappearance)} = \phi_{ARH} + 2\phi_{RR} + (\phi_{RH} + \phi_{R(-H)}) + \phi_4 \qquad (13)$$

$$\phi_{A^{-\bullet}} = k_{ET}[\text{borate}]/(k_{ET}[\text{borate}] + k_f) \qquad (14)$$

$$A_{inf}/A(0) = [2\phi_{RR} + (\phi_{RH} + \phi_{R(-H)})]/[\phi_{ARH} + 2\phi_{RR} + (\phi_{RH} + \phi_{R(-H)})] \qquad (15)$$

In the preparative laser-flash experiments with DCN and $PhCH_2B(Ph)_3^-$, (see results for experiments FP1 and FP2 in Table 2), the average quantum yield of $DCN^{-\bullet}$ formation $<\phi_{A^{-\bullet}}> = 0.22$ is in reasonable agreement with $\phi_{A^{-\bullet}} = 0.29$ calculated from eqn. (14) with an initial ET rate between DCN* and *n*-butyltriphenylborate $k_{ET} = 2 \times 10^9$ M^{-1} s^{-1} [18] and the florescence rate of the DCN*, $k_f = 1/\tau_f = 1 \times 10^8$ s^{-1}.[24] In a typical kinetic experiment with DCN and $PhCH_2B(Ph)_3^-$, $A(0) = 0.12$ and $A_{inf} = 0.65$ were obtained. When we apply these numbers together with $<\phi_{RR}> = 0.055$, $(\phi_{RH} + \phi_{R(-H)}) = 0$ for benzyl radicals and $<\phi_{ARH}> = 0.11$ (Table 2), a fairly good agreement is obtained between $A_{inf}/A(0) = 0.4$ and $2\phi_{RR}/(\phi_{ARH} + 2\phi_{RR}) = 0.5$ as predicted by eqn. (15). The initial absorption $A(0)$ of the above mentioned kinetic experiment with DCN and $PhCH_2B(Ph)_3^-$ may be calculated based on the number of photons that enter the quartz cell = 5.56×10^{-8} mol, the absorbance = 0.55 of the solution, the effective reaction volume of the cell $V = 0.3$ cm^3, $<\phi_{A^{-\bullet}}> = 0.22$ and the extinction coefficient of the radical anion of DCN, $\varepsilon_{DCN} = 3578$ M^{-1} cm^{-1} (Table 1). When we apply these numbers, $A(0) = 0.12$ may be calculated, which is in perfect agreement with the experimentally observed value. The values of ϕ_{RR} vary with the irradiation method between 0 and 0.060. In the steady-state photolysis and in the laser-flash experiments with the YAG laser with a 10 Hz pulse repetition rate a certain steady-state concentration of $DCN^{-\bullet}$ builds up and causes a suppression of the RR dimerization reaction. In the laser-flash photolysis experiments FP1 and FP2 (Table 2) an excimer laser was applied with a 0.1 Hz repetition rate and with time for vigorous shaking of the cell after every 5 to 10 pulses. In these two experiments the buildup of $DCN^{-\bullet}$ is much smaller than in the other photolysis experiments. Finally, it is seen from Table 2 that the product and photon mass balance expressed by eqn. (13) are reasonably fulfilled. In conclusion, the above analysis shows that the mechanism defined by eqns. (5)–(11) gives a valid description of the reaction.

Kinetic measurements

A second order kinetic decay curve was fitted to the recorded decay as shown in Fig. 1 and the initial absorbance $A(0)$, A_{inf} and the apparent second order rate constant k were obtained. As seen from Fig. 1, the fitted curve represents the experimental curve very well. From the second order fit parameters it is possible to calculate the two rate constants k_1 and $(k_9 + k_{10})$ by eqns. (22), (25) and (26) (shown in the appendix).

The results of the laser-flash experiments are shown in Tables 3 and 4. The optical density of these experiments was close to 0.50. Ideally, the optical density should be kept as low as possible in order to obtain a reaction mixture with $A^{-\bullet}$ and R· concentrations as homogeneous as possible. However, in order to obtain sufficiently high initial absorptions [$A(0) > 0.05$] a compromise had to be made. With an od = 0.5 the intensity of the laser beam is reduced to 32% through the reaction cell. The absorption trace observed is therefore a complicated average of an initial inhomogeneous radical distribution in the reaction

Table 3 Kinetic data of the reactions $A^{-\bullet} + R^{\bullet} \longrightarrow AR^{-}$ (k_1) and $R^{\bullet} + R^{\bullet} \longrightarrow RR + RH + (R{-}H)$ ($k_9 + k_{10}$) obtained by laser-flash photolysis on a solution of A and $RB(Ph)_3^{-}\ N^{+}(CH_3)_4$ in DMF

A	R	$\lambda_{A^{-\bullet}}$/nm	Absorbance (351 nm)	$k_1 \times 10^{-9}$ M^{-1} s^{-1}	$(k_9 + k_{10}) \times 10^{-9}$ M^{-1} s^{-1}	Average of $(k_9 + k_{10}) \times 10^{-9}$ M^{-1} s^{-1}
DCN[a]	Methyl	512	0.49	1.8	1.0	
DCA[b]	Methyl	520	0.48	2.0	2.2	1.4
FLUO[c]	Methyl	550	0.55	2.4	0.9	
DCN	*n*-Butyl	512	0.49	2.9	1.7	
DCA	*n*-Butyl	520	0.48	2.8	1.6	1.6
FLUO	*n*-Butyl	550	0.55	1.5	1.4	
DCN	*sec*-Butyl	512	0.49	1.9	1.1	
DCA	*sec*-Butyl	520	0.48	1.8	1.3	1.1
FLUO	*sec*-Butyl	550	0.55	0.8	0.8	
DCN	*tert*-Butyl	512	0.42	2.1	1.1	
DCA	*tert*-Butyl	520	0.24–0.55	1.9	1.2	1.4
FLUO	*tert*-Butyl	550	0.49	1.4	2.0	
DCN	Benzyl	512	0.42	2.0	0.6	
DCA	Benzyl	520	0.48	1.5	1.3	0.9
FLUO	Benzyl	550	0.55	1.6	0.7	

[a] DCN: 1,4-dicyanonaphthalene. [b] DCA: 9,10-dicyanoanthracene. [c] FLUO: fluorenone.

Table 4 Rate constants k_1 and ($k_9 + k_{10}$) obtained as a function of the absorbance of a solution of fluorenone and *n*-BuB(Ph)$_3^-$ N$^+$(CH$_3$)$_4$ in DMF. Detection wavelength was 550 nm

od (351 nm)	$k_1 \times 10^{-9}$ M^{-1} s^{-1}	$(k_9 + k_{10}) \times 10^{-9}$ M^{-1} s^{-1}
0.12	1.87	1.44
0.24	1.80	1.49
0.49	1.57	1.38
0.49	1.15	1.49
0.50	1.59	1.43
0.50	1.15	1.27
0.50	1.59	1.43
Average	1.53 ± 0.26	1.42 ± 0.07

cell. The inhomogeneity effect is reduced, however, because the effective laser-beam light path from which the flash lamp light is collected by the monochromator is much less than 1 cm. In order to investigate the inhomogeneity effect on the rate constants k_1 and ($k_9 + k_{10}$), a series of experiments were performed in which the optical density was varied between 0.16 and 1. As seen from Table 4 the reproducibility of the rate data at constant absorbance is in the range from 20 to 30%. The variation of the k_1 rate data is below 30% when absorbance is changed between 0.16 and 0.55 and the data do not show any systematic trend. The reproducibility of the data obtained with low absorbance is less than that with the higher absorbance probably due to the lower signal to noise ratios. This may explain some of the variation observed. The uncertainty of the k_1 rate data obtained at absorbance = 0.5 is estimated to be about ±30%.

In general, radical anions may react either with radicals by the coupling reaction [eqn. (1)] or by an electron transfer reaction [eqn. (16)]

$$A^{-\bullet} + R\cdot \xrightarrow{k_{16}} A + R^{-} \qquad (16)$$

The reduction potentials of *n*-, *sec*- and *tert*-butyl radicals are far more negative ($E_{1/2} < -2.2$ V *vs.* SCE)[5] than the redox potentials of the three acceptor molecules. This means that the electron transfer reaction [eqn. (16)] is much slower than the coupling reaction [eqn. (1)] and the competition parameter $q = k_{16}/(k_1 + k_{16})$ is therefore ≈ zero. The reduction potentials of the methyl and benzyl radicals are −1.78 and −1.42 V *vs.* SCE, respectively;[5] however the q values are still close to zero for the radical anions used in this work which all have standard potentials of 200 mV more positive than $E_{1/2}$ of the benzyl radical. Electron transfer between $A^{-\bullet}$ and R· is therefore not important for the acceptors used in this work.

Discussion of rate constants

As seen from Table 3 the coupling rates between the three aromatic radical anions and methyl, *n*-, *sec*-, *tert*-butyl and benzyl radicals are nearly equal and fall in the range $0.8 \times 10^9 < k_1 < 2.9 \times 10^9$ M^{-1} s^{-1} with an average rate constant $k_1 = 1.9 \times 10^9$ M^{-1} s^{-1}. A similar average value $k_1 = 1.4 \times 10^9$ M^{-1} s^{-1} was obtained by indirect methods between *n*-, *sec*- and *tert*-butyl radicals and the aromatic radical anions of anthracene, *p*-diacetylbenzene and *p*-dicyanobenzene.[11] The coupling rates of the methyl radical and *n*-butyl radicals might be expected to be faster than those of the more steric hindered *tert*-butyl radical; however, the results of the present and previous works[10,11] show that k_1 is insensitive to the steric crowding of the radical. The benzyl radical is, in general, less reactive than alkyl radicals but the difference in electronic properties of the alkyl and benzyl radicals is not reflected in the k_1 values. Furthermore only small and non-systematic variation of k_1 is observed by changing the structure and redox potential of the aromatic radical anion.[25] It is therefore reasonable to use an average k_1 value for all mediators and radicals in the calculation of standard redox potential from measured reduction potentials obtained by the indirect q-plot method.[12–15] If $k_1 = (2 \pm 1) \times 10^9$ M^{-1} s^{-1} is used in the expression of the correction term $H_{corr} = E^0{}_{R^\bullet/R^-} - E_{1/2}$ (see ref. 14) the uncertainties of the calculated standard potentials due to the k_1 variation will be ±40 mV for benzyl radicals with self-reorganization energies $\lambda(0) = 10$ kcal mol^{-1} and ±70 mV for alkyl radicals with $\lambda(0) = 50$ kcal mol^{-1}.

Radical–radical dimerization + disproportionation rates ($k_9 + k_{10}$) were obtained in the range of 0.6×10^9 to 2×10^9 M^{-1} s^{-1} (see Table 3). For a certain radical the ($k_9 + k_{10}$) values should be constant and independent of the aromatic compound. This is, however, only observed in the experiments with *n*-butyl and *sec*-butyl radicals. The low precision of the determination of the ($k_9 + k_{10}$) values is probably due to the fact that ($k_9 + k_{10}$) is sensitive to small variations in the A_{inf} values [see eqn. (23) in the appendix] and A_{inf} is sensitive to small amounts of impurities, *e.g.* oxygen. For benzyl radicals the disproportionation reaction is slow and $(k_9 + k_{10}) \sim k_9 = 0.9 \times 10^9$ M^{-1} s^{-1}. Disproportionation of *tert*-butyl radicals in pentane to give isobutane and isobutene is *ca.* 7 times faster than the dimerization reaction.[26] Disproportionation is also important for secondary ($k_{10}/k_9 = 1$) and to some extent for primary alkyl radicals too ($k_{10}/k_9 = 0.15$).[26,27]

Conclusion

A number of coupling rates between methyl, butyl and benzyl radicals and three aromatic radical anions have been obtained by a new laser-flash photolysis method. For the first time, coupling rates between methyl and benzyl radicals and aromatic radical anions have been obtained. An average value $k_1 = 1.9 \times 10^9$ M^{-1} s^{-1} was found with a relatively small variation of the k_1 values ($0.8 - 2.9 \times 10^9$ M^{-1} s^{-1}). The results demonstrate that the coupling rate k_1 is insensitive to changes in the steric and electronic properties of the radicals and the structure and standard potentials of the aromatic radical anions. An interesting by-product **4** was detected in the laser-flash experiments with 1,4-dicyanonaphthalene. The reaction is likely to take place in the solvent cage by an initial photoinduced ET process between dimethylformamide and 1,4-dicyanonaphthalene, as formulated in eqn. (11).

Experimental

Materials

Fluorenone and 9,10-dicyanoanthracene were obtained from Aldrich. 1,4-Dicyanonaphthalene was synthesized according to the method of Heiss.[28] The alkyl- and benzyltriphenylborates were prepared by the reaction of alkyl lithium with triphenylboron according to references given.[16,29] The borates were isolated either as their tetramethyl or tetrabutylammonium salts.[19] Dimethylformamide was obtained from AKZO and used as received.

Kinetic experiments

Time-resolved absorption measurements were carried out by laser-flash photolysis in solution at room temperature. The experiments were performed in a 10 × 10 mm^2 Hellma quartz cell equipped with a glass adapter for Schlenk-flask operation.

In a typical experiment the borate salt (0.050–0.075 mmol) was transferred to the cell and the solution of the acceptor compound (3.41 ml) in dimethylformamide was added with a concentration corresponding to an absorbance of 0.2 to 0.57 at 351 nm. The cell was connected to a vacuum line (< 0.1 mmHg) and oxygen was removed from the solution by means of three freeze–pump–thaw cycles. The solutions were photolyzed by a laser pulse at 351 nm (90–130 mJ, 20 ns) from an excimer laser (Lambda Physik LPX 220i). The transient absorption at right angles to the exciting laser beam was monitored by means of a pulsed Xe lamp (Varian VIX150UV), a monochromator (McPherson 2035), and a photomultiplier (1P28). Transient data were stored on a digital oscilloscope (LeCroy 9450) and handled in a PC using custom made software. After firing the laser, the absorbance of the sample as function of time was obtained at a wavelength in the visible part of the radical anion spectrum. A second order decay curve was fitted to the trace by the computer, and the absorbance at time zero [$A(0)$] and infinitive time (A_{inf}) and the apparent second order rate constant k were obtained. Five traces were recorded and the average second order parameters $<A(0)>$, $<A_{\mathrm{inf}}>$ and $<k>$ obtained and used for the kinetic rate data calculations (see Appendix).

Preparative photolysis

The photolysis samples were prepared in a Hellma quartz cell as described above. Three irradiation sources were applied: an excimer laser (λ = 351 nm, 90–130 mJ pulse^{-1}), a Nd : YAG-laser (Continuum, Powerlite PL9010) (λ = 355 nm, 10–20 mJ pulse^{-1}) and a 500 W tungsten–xenon lamp mounted in an Oriel lamp house. In the steady-state photolysis the light was filtered through a water-cooling jacket, a 305 nm bandpass filter and an Oriel 321 ± 5 nm filter. The light exposure was obtained by Aberchrome 540 actinometry in all the experiments.[30] After irradiation tetradecane was added as an internal standard and the solution was extracted with diethyl ether (10 ml) and water (10 ml). The diethyl ether phase was separated, washed with water (10 ml) and dried by molecular sieves (4 Å). Finally, the ether extract was analyzed by a Hewlett Packard 5890 A gas chromatograph equipped with a 5971A MSD. A HP5 25 m, 0.25 mm id GC-column was used, injection temperature 250 °C, helium flow 1.0 ml min^{-1}, temperature program 100 °C in 2 min to 300 °C, rate 10 °C min^{-1}.

Extinction coefficient

The extinction coefficient of the 1,4-dicyanonaphthalene radical anion was obtained according to the method described by Pedersen *et al.*[11,19]

Identification of products

The ^{1}H and ^{13}C-NMR spectra were recorded with a Bruker 250 MHz spectrometer. J values are given in Hz.

Tetramethylammonium *n*-butyltriphenylborate: δ_{H}(250 MHz; DMSO-d6; Me$_4$Si) 0.76 (t, 3H, J 7.3), 0.92 (m, 4H), 1.22 (quintet, 2H, splitting = 7.06), 3.07 (s, 12 H), 6.4 (t, 3H, J 7.25), 6.89 (t, 6H, J 7.2), 7.20 (d, 6H, J 6.8). δ_{C}(62.5 MHz; DMSO-d6; Me$_4$Si) 14.7, 27.6, 27.6 (q, $^1J_{\mathrm{C-B}}$ = 49), 30.4, 54.4 (t, $^1J_{\mathrm{CN}}$ 4.2), 121.2, 125.4, 134.5, 166.8 (q, $^1J_{\mathrm{CB}}$ 49).

Tetramethylammonium *sec*-butyltriphenylborate: δ_{H}(250 MHz; DMSO-d6; Me$_4$Si) 0.59 (d, 3H, J 6.3), 0.85 (t, 3H, J 7.3), 1.35 (broad, 1H), 1.55 (m, 2H), 3.07 (s, 12H), 6.77 (t, 3H, J 7.2 Hz), 6.9 (t, 6H, J 7.5), 7.29 (t, 6H, J 7.2). δ_{C}(62.5 MHz; DMSO-d6; Me$_4$Si) 15.5, 16.7, 27.4 (q, $^1J_{\mathrm{C-B}}$ 42), 27.8, 55.1 (t, $^1J_{\mathrm{CN}}$ 4.2), 123.2, 126.2, 135, 165 (q, $^1J_{\mathrm{CB}}$ 47).

Tetramethylammonium *tert*-butyltriphenylborate : δ_{H}(250 MHz; DMSO-d6; Me$_4$Si) 0.83 (broad, 9H), 3.07 (s, 12 H), 6.8 (t, 3H, J 7.2), 6.91 (t, 6H, J 7.25), 7.25 (m (broad line), 6H). δ_{C}(62.5 MHz; DMSO-d6; Me$_4$Si) 34.0, 54.4 (t, $^1J_{\mathrm{CN}}$ 4.1), 121.0, 122.0, 124.6, 126.8, 125.32, 132.8, 136.0, 164.9 (q, $^1J_{\mathrm{CB}}$ 49).

Tetramethylammonium methyltriphenylborate: δ_{H}(250 MHz; DMSO-d6; Me$_4$Si) 0.31 (broad, 3H), 3.15 (s, 12 H), 6.9 (m, 1H), 7.0 (m, 2H), 7.3 (broad, 1H). δ_{C} (62.5 MHz; DMSO-d6; Me$_4$Si) 14.2 (q, $^1J_{\mathrm{C-B}}$ 42), 54.4 (t, $^1J_{\mathrm{CN}}$ 4.2), 121.2, 125.3, 134.0, 166.8 (q, $^1J_{\mathrm{CB}}$ 48.6).

Tetramethylammonium benzyltriphenylborate: δ_{H}(250 MHz; DMSO-d6; Me$_4$Si) 2.4(broad, 2H), 3.05(s,12 H), 6.5 (t, 2H, J 7.4), 6.8 (m, 6H), 6.9 (t, 6H, J 7.1), 7.2 (broad, 6H). 7.28 (m (broad line), 6H). δ_{C} (62.5 MHz; DMSO-d6; Me$_4$Si) 47 (q, $^1J_{\mathrm{C-B}}$ 49), 54.4 (t, $^1J_{\mathrm{CN}}$ 4.2), 120.5, 121.3, 125.2, 125.8, 127.2, 134.69, 150.9, 163.8 (q, $^1J_{\mathrm{CB}}$ 49.9).

3-benzyl-1-cyanonaphthalene **2a**: *m*/*z* 244 (20%); 243 (M$^+$,100); 242 (56); 228 (16); 227 (14); 215 (22).

4-benzyl-1-cyanonaphthalene **3a**: *m*/*z* 244 (10%); 243 (M$^+$,100); 242 (74); 228 (37); 227 (18); 215 (27).

3-butyl-1-cyanonaphthalene **2b**: *m*/*z* 209 (M$^+$, 38%); 167 (69); 166 (100); 153 (10); 140 (23); 139 (15).

4-butyl-1-cyanonaphthalene **3b**: *m*/*z* 209 (M$^+$, 34%); 168 (10); 167 (91); 166 (100); 140 (24); 139 (15).

The cyanonaphthalene substituted in the 3-position is the major coupling isomer according to Lan and Schuster.[16,17]

4-cyano-*N*,*N*-dimethylnaphthalene-1-carboxamide **4**: *m*/*z* 224 (M$^+$, 80%); 223 (37); 207 (100); 195 (18); 167 (37); 166 (47); 140 (24).

Appendix

The laser instrument software approximates the observed decay of the radical anion concentration with a simple second order decay expression eq 17:

$$[\mathrm{A}^{-\bullet}] = (1/\varepsilon)\,[A_{\mathrm{inf}} + A/(1 + k\,t\,A)] \qquad (17)$$

$A(0) = (A + A_{\mathrm{inf}})$ is the absorption at $t = 0$ and, A_{inf} the absorption at $t = \infty$ and k is the second order rate constant. The decay mechanism of A$^{-\bullet}$ is assumed to follow the three reactions eqns. (1), (9) and (10). The decay is determined by the differential equations eqn. (18) and eqn. (19):

$$d[A^{-\bullet}]/dt = k_1 [A^{-\bullet}][R^\bullet] \tag{18}$$

$$d[R^\bullet]/dt = (k_9 + k_{10}) [R^\bullet][R^\bullet] \tag{19}$$

[R·] may be calculated from A, A_{inf} and k by substituting eqn. (17) in eqn. (18):

$$[R\cdot] = (1/k_1) (A^2 k/(1 + A k t)^2) [A_{inf} + A/(1 + Akt)]^{-1} \tag{20}$$

At $t = 0$,

$$[R^\bullet] = [A^{-\bullet}] = (1/\varepsilon) (A_{inf} + A) \tag{21}$$

The rate constant k_1 may be isolated by inserting $t = 0$ in eqn. (20) and combining with eqn. (21):

$$k_1 = \varepsilon A^2 k/(A + A_{inf})^2 \tag{22}$$

At $t \longrightarrow \infty$

$$[RR] + [RH] + [R(-H)] = A_{inf}/2\varepsilon \tag{23}$$

The final concentration of [RR] + [RH] + [R(–H)] may be obtained by the integration of eqn. (19). If we combine it with eqn. (23), it gives:

$$([RR] + [RH] + [R(-H)])_{inf} = A_{inf}/2\varepsilon = \int (k_9 + k_{10}) [R^\bullet]^2 dt \tag{24}$$

An expression of $(k_9 + k_{10})$ may be derived by combining eqn. (20) with eqn. (24):

$$(k_9 + k_{10}) = k_1^2/(2b^3 k \varepsilon I) \tag{25}$$

$$b = A/A_{inf} \tag{25a}$$

$$I = \int_1^\infty 1/(x^2(x+b)^2)dx, \ x = (1 + Akt) \tag{25b}$$

An analytical solution to the integral is shown in eqn. (26).

$$I = (b + 2)/b^2 (b + 1) - (2/b^3) \ln(b + 1) \tag{26}$$

References

1 J. Simonet, M.-A. Michel and H. Lund, *Acta Chem. Scand. B*, 1975, **B29**, 489.

2 H. Lund and J. Simonet, *J. Electroanal. Chem.*, 1975, **65**, 205.

3 H. Lund, *J. Mol. Catal.*, 1986, **38**, 203.

4 H. Lund, K. Daasbjerg, D. Occhialini and S. U. Pedersen, *Russian J. Electrochem.*, 1995, **31**, 865.

5 H. Lund, K. Daasbjerg, T. Lund, D. Occhialini and S. U. Pedersen, *Acta Chem. Scand.*, 1997, **51**, 135.

6 M. F. Nielsen and O. Hammerich, *Acta Chem. Scand.*, 1987, **B41**, 668.

7 K. Daasbjerg and T. B. Christensen, *Acta Chem. Scand.*, 1995, **49**, 128.

8 J. F. Garst, *Acc. Chem. Res.*, 1971, **4**, 400.

9 J. F. Garst and C. D. Smith, *J. Am. Chem. Soc.*, 1976, **98**, 1520.

10 S. U. Pedersen and T. Lund, *Acta Chem. Scand.*, 1991, **45**, 397.

11 S. U. Pedersen, T. Lund, I. Fussing, K. Daasbjerg and H. Lund, *Acta Chem. Scand.*, 1998, **52**, 657.

12 R. Fuhlendorff, D. Occhialini, S. U. Pedersen and H. Lund, *Acta Chem. Scand.*, 1989, **43**, 803.

13 D. Occhialini, S. U. Pedersen and H. Lund, *Acta Chem. Scand.*, 1990, **44**, 715.

14 D. Occhialini, J. S. Kristensen, K. Daasbjerg and H. Lund, *Acta Chem. Scand.*, 1992, **46**, 474.

15 K. Daasbjerg, S. U. Pedersen and H. Lund, in *General Aspects of the Chemistry of Radicals*, ed. Z. B. Alfassi, John Wiley & Sons, 1999, 385–427.

16 J. Y. Lan and G. B. Schuster, *J. Am. Chem. Soc.*, 1985, **107**, 6710.

17 J. Y. Lan and G. B. Schuster, *Tetrahedron Lett.*, 1986, **27**, 4261.

18 G. B. Schuster, *Pure & Applied. Chem.*, 1990, **62**, 1565.

19 S. U. Pedersen, T. B. Christensen, T. Thomasen and K. Daasbjerg, *J. Electroanal. Chem.*, 1998, **454**, 123.

20 T. Lund, *Acta Chem. Scand.*, 1996, **50**, 64.

21 A. Y. Polykarpov and D. C. Neckers, *Tetrahedron Lett.*, 1995, **36**, 5483.

22 M. P. Fontaine-Aupart, M. Frejacques, E. Renault, C. Ferradini, M. Gardes-Albert, B. Hickel, C. Rivalle and E. Bisagni, *J. Photochem. Photobio. B*, 1993, **21**, 203.

23 J. F. O'Donnel and C. K. Mann, *J. Electroanal. Chem.*, 1967, **13**, 157.

24 D. R. Arnold and A. J. Maroulis, *J. Am. Chem. Soc.*, 1976, **98**, 59.

25 A referee suggested that the uniform k_1 rate constants could reflect cage recombination of $A^{-\bullet}$ and $R^\bullet$. However, Schuster et al. demonstrated in 1986 (ref. 18) that the coupling of the radical $R^\bullet$ and the radical anion $A^{-\bullet}$ took place in the solution. If the coupling had occurred 100% in the solvent cage we would not have seen any signal in the nsec. laser-flash experiment. The perfect match between the observed initial absorption A(0) = 0.12 of Fig. 1 and the calculated value (see text) further confirm Schuster's conclusion. Even if a minor percentage of the coupling had taken place inside the solvent cage this would not harm the kinetic analysis.

26 R. A. Sheldon and J. K. Kochi, *J. Am. Chem. Soc.*, 1970, **92**, 4395.

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28 L. Heiss and E. F. Paulus, *Liebigs Ann. Chem.*, 1980, 1583.

29 R. J. Damico, *J. Org. Chem.*, 1964, **29**, 1975.

30 H. G. Heller and J. R. Langan, *J. Chem. Soc.*, *Perkin Trans. 2*, 1981, **341**, 42.

31 A. F. Olea, D. R. Worrall, F. Wilkinson, S. L. Williams and A. A. Abbdel-Shafi, *Phys. Chem.*, 2002, **4**, 161.