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Ionization of Cyclic Aromatic Amines by Free Electron Transfer: Products Are Governed by Molecule Flexibility

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The bimolecular electron transfer from secondary aromatic amines to parent radical cations of nonpolar solvents such as alkanes and alkyl chlorides results in the synchronous formation of amine radical cations as well as aminyl radicals, in comparable amounts. If as for cyclic aromatic amines (c-Ar_2NH) the intramolecular bending motion around the amine group is restricted in varying degrees (acridane, phenothiazine) or completely prevented (carbazole), then this picture is modified. In the free electron transfer, the completely rigid carbazole yields exclusively amine radical cations. Acridane exhibits preferred radical cations, but phenothiazine with the more flexible six-membered ring involving sulfur as a further heteroatom follows the common two-product rule; see above. The phenomenon is reasoned by a peculiarity in the bimolecular free electron transfer where after diffusional approach the actual electron jump proceeds in the ultrashort time range. Therefore, it reflects femtosecond molecular motions which, in the case of free mobility, continuously pass through different molecule conformers, combined with fluctuation of the electrons of the responsible molecular n-orbitals. The rigid systems, however, do not show this effect because of a nonexistent bending motion.

Introduction

In the past few years, a new electron-transfer phenomenon has been reported named free electron transfer (FET).[1,2] It stands for the bimolecular electron transfer from a diversity of donors to parent radical cations derived from saturated nonpolar solvents such as alkanes, alkyl chlorides, etc. The most appropriate technique for generating and observing such radical cations ($RX^{\bullet+}$) is electron pulse radiolysis; see eq 1. In the presence of electron donors, a rapid diffusion-controlled electron transfer takes place which exhibits for some electron donors (phenols,[2,3] thiophenols,[4] selenols,[5] aromatic amines,[6] benzyltrimethylsilanes,[7,8] etc.) a surprising product distribution, that is, a direct and synchronous formation of radical cations and of corresponding radicals. This is demonstrated for the case of aniline-type compounds[6] (Ar−NHR); see Scheme 1.

$$RX \rightarrow \text{vvv} \rightarrow RX^{\bullet+} + e_{solv}^{-} \qquad X = H, Cl \qquad (1)$$

For X = Cl

$$RX + e_{solv}^{-} \rightarrow R^{\bullet} + Cl^{-} \qquad (2)$$

Both products are given in boldfaced type. Their synchronous generation is explained in terms of a mechanism where after diffusional approach the real electron jump proceeds in extremely short times estimated to a few femtoseconds or less. Therefore, bending motions of the $Ar-\curvearrowleft-NHR$ group ($\nu \approx 10^{13}$ Hz) are recognized insofar that the different electron distributions in the intermediate conformer mix are identified by the formation of different products. As for the two borderline cases such as a planar (mesomeric) and a twisted structure, resonance-stabilized radical cations and N-centered ones are formed, respectively. The mesomeric, planar radical cation overcomes into the nanosecond and mircrosecond time range whereas the localized cationic structure immediately deprotonates, assisted by the solvent. Recently, a rapid deprotonation of aniline-type radical cations with a slightly twisted aminyl group was reported[9] which seems to be in line with our observation. In combination with the quantum chemical calculation of the molecular dynamics, the pulse radiolysis data give a strong indication for these processes. This turned out to be a general phenomenon for all those scavenger molecules exhibiting marked bending motions and product radical cations of very different stability.

Now the question arises whether a restricted bending motion caused by a limited flexibility around the amine group may affect the product situation. For *o*-hydroxybenzoates[10] it was found that strong hydrogen bonding prevents the mobility of the phenol group, and indeed exclusively radical cations have been formed. In the present paper, we report about the ionization of cyclic aromatic amines (c-Ar_2NH) by free electron transfer. The studied molecules are acridane and phenothiazine as six-membered ring structures with restricted mobility and carbazole where no bending motion is expected, because of the rigid five-membered ring.

Experimental Section

Pulse radiolysis experiments were performed with high-energy electron pulses (1 MeV, 15 ns duration) generated by a pulse transformer accelerator ELIT (Institute of Nuclear Physics, Novosibirsk, Russia). The absorbed dose per pulse measured with an electron dosimeter was between 50 and 100 Gy, corresponding to transient concentrations around 10^{-5} mol dm^{-3}. Details of the pulse radiolysis setup are reported elsewhere.[3]

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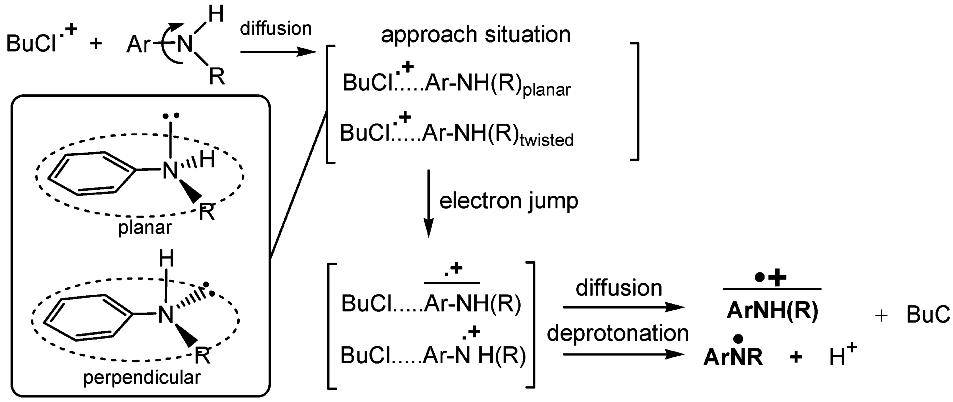
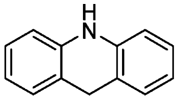
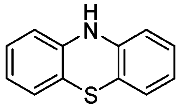
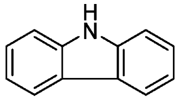
SCHEME 1: Mechanism of FET Involving Anilines: R = H, Me, Ph



The solvent *n*-butyl chloride was purified as reported.[9] The spectrograde substances from Aldrich and Merck were generally dried using molecular sieve chromatography. The amines were of maximum commercial grade (Merck) and used as received. The following amines have been used for our study


acridane


phenothiazine


carbazole

The kinetic simulations of the superimposed transient absorption time profiles were performed using modified versions of the program ACUCHEM[11] which numerically solves the differential equation for the assumed reaction mechanism.[3] To adjust the concentration profiles to those of optical absorption, reasonable extinction coefficients were used which were determined independently, for example, by one-electron oxidation in aqueous solution. Quantum chemical calculations were performed with the density functional theory hybrid B3LYP with 6-31G(d) basis set using Gaussian 03.[12−14] This enabled vibrational analysis of the studied molecules and geometric calculation of frontier orbitals. The transient spectra were calculated with unrestricted time-dependent DFT[15] at the B3LYP/6-31+G(d,p) level.

Results

Pulse Radiolysis with Phenothiazine Solutions. We used *n*-butyl chloride as the solvent for the pulse radiolysis experiments. In this case, the electron transfer could be well investigated because the parent radical cation $C_4H_9Cl^{\bullet+}$ has a convenient lifetime of about 130 ns.[6] Adding millimolar concentrations of the amines, the decay of the $C_4H_9Cl^{\bullet+}$ signal is accelerated according to a pseudo-first-order reaction. The rate constant was determined to be $k_2 = 1.5 \times 10^{10}$ dm^3 mol^{-1} s^{-1}.

The product transients of the amines appear simultaneously with the decay of the solvent radical cation. Figure 1 shows the product transient spectra taken after pulsing a deoxygenated solution of 5×10^{-3} mol dm^{-3} phenothiazine in *n*-butyl chloride. The spectrum taken at the earliest time shows two peaks with $\lambda_{max} = 435$ and 520 nm.

From the kinetic behavior and from the spectra taken at different times after the pulse, the transient absorptions can be identified as caused by a phenothiazine radical cation (520 nm) and by the corresponding amine radical (two peaks, 435 and 520 nm), respectively. A solution containing an additional 0.1 mol dm^{-3} DMSO shows only both aminyl radical peaks (not shown here), in the same proportion as it exhibits after the cation decay (3.5 μs); see Figure 1. That means that dimethyl sulfoxide (DMSO) quenched the phenothiazine radical cation completely and selectively by a mechanism which is discussed later.

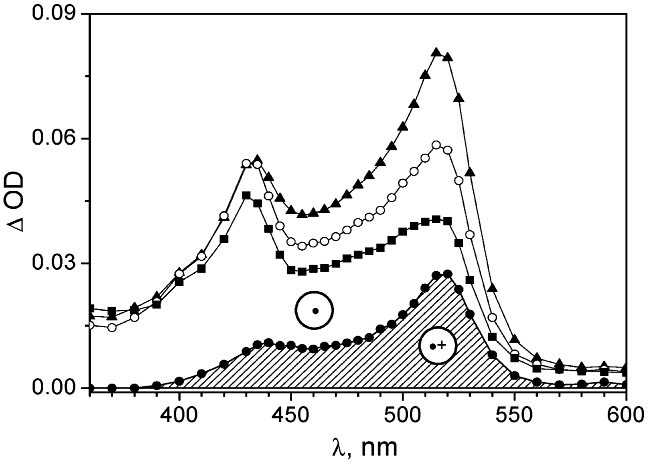


Figure 1. Transient spectra obtained by pulse radiolysis of 5 mol dm^{-3} phenothiazine in deaerated *n*-butyl chloride. Spectra correspond to times (▲) 130 ns, (○) 1 μs, and (■) 3.5 μs after the pulse. The spectrum of the radical cation (●) is given as a difference between (▲) and (■).

For the original sample, although the absorptions of the species are very superimposed, the time profiles taken at 520 and 430 nm show that both transients were formed rapidly. But with the decay of the radical cation (520 nm), a further part of the amine radical is formed (430 nm). From the latter one it can be clearly seen that a considerable part of the aminyl radical is formed immediately in the course of FET, whereas a distinct part grows in a delayed manner. The delayed generation of amine radicals happens by deprotonation caused by a reaction with the strong nucleophile Cl$^-$ (reaction 3). This is supported by the finding that adding chloride in the form of tetrabutylammonium chloride accelerates the deprotonation considerably.

$$\text{c-Ar}_2\text{NH}^{\bullet+} + \text{Cl}^- \rightarrow \text{c-Ar}_2\text{N}^{\bullet} + \text{HCl}$$
$$k = 5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \qquad (3)$$

Acridane as Electron Donor. Although less characteristic from the spectral side, the situation for acridane could also be analyzed well. Figure 3 shows transient spectra taken after pulsing a solution of 5×10^{-3} mol dm^{-3} acridane in *n*-butyl chloride. On the basis of the spectra taken at different times and considering the influence of additional chloride (in the form of n-Bu$_4$N$^+$Cl$^-$, reactions 3 and 5), the following assumptions can be made: The broad peak between 550 and 700 nm

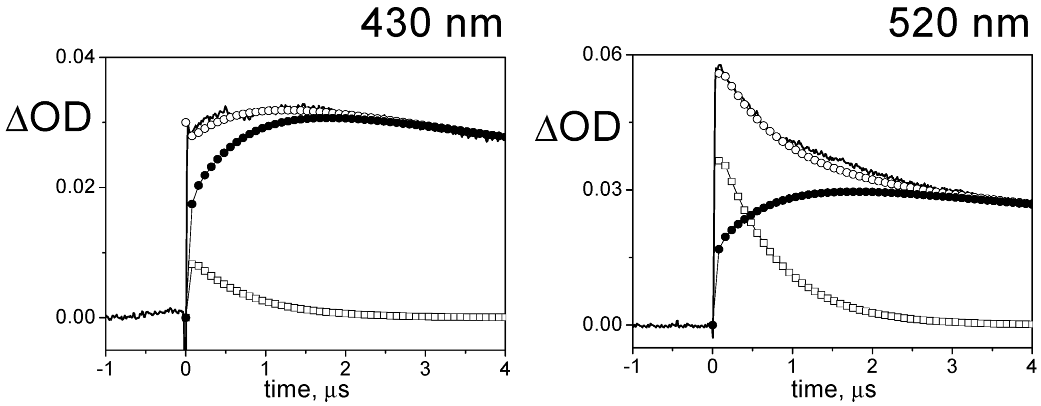


Figure 2. Simulation of the experimental time profiles obtained after pulsing a deaerated solution of 2×10^{-3} mol dm^{-3} in *n*-butyl chloride: (−) experimental profile, (○) simulated profile, (●) phenothiazine radical, and (□) phenothiazine radical cation.

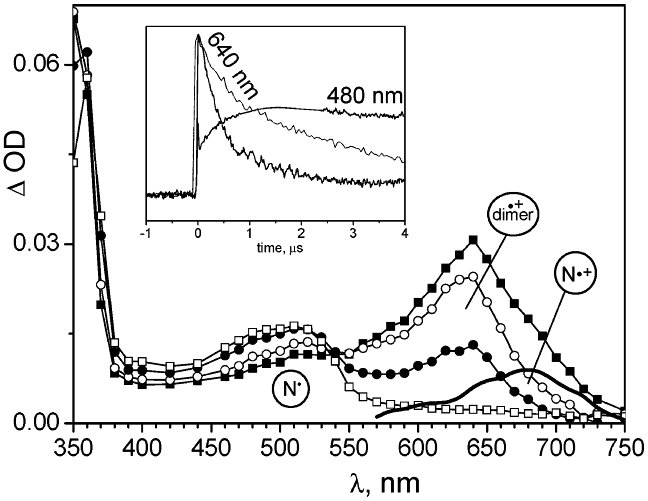


Figure 3. Transient spectra taken after pulsing a N_2 purged solution of 2×10^{-3} mol dm^{-3} acridane and 9×10^{-4} mol dm^{-3} *n*-Bu_4NCl in *n*-BuCl: (■) 86 ns, (○) 190 ns, (●) 520 ns, and (□) 3.5 μs. The spectrum of the acridane radical cation (bold line) is taken as the difference between (■) and (○). Experimental time profiles are given as inset. The pointed profile was taken from a solution without *n*-Bu_4NCl.

originates from a superposition of the absorptions of the amine radical cation ($\lambda_{max} \approx 680$ nm) and those of a dimer radical cation ($\lambda_{max} \approx 640$ nm). This is formed by a charge-transfer interaction of the amine radical cation with the parent amine molecule. Such dimers are usually generated in an equilibrium (4) and have been observed for triphenylamine[6] and also a variety of other aromatic compounds.[24,25]

$$\text{c-Ar}_2\text{NH}^{\bullet+} + \text{c-Ar}_2\text{NH} \leftrightarrows (\text{c-Ar}_2\text{NH})_2^{\bullet+} \qquad (4)$$

$$(\text{c-Ar}_2\text{NH})_2^{\bullet+} + \text{Cl}^- \rightarrow \text{c-Ar}_2\text{N}^{\bullet} + \text{c-Ar}_2\text{NH} + \text{HCl}$$

$$k \approx 10^9 \text{ dm}^{-3} \text{ mol}^{-1} \text{ s}^{-1} \qquad (5)$$

The small and broad peak around 510 nm is caused by the acridane aminyl radical. Because of spectral superpositions, from the kinetic point of view, the time profiles are difficult to analyze. To some extent it seems to be formed rapidly in FET. But the very dominant part originates from the delayed deprotonation of the amine radical cation (3) and its dimer (5). This can be seen well in the inset in Figure 3 where the influence of additional chloride is demonstrated and the deprotonation gets faster and more efficient. The decays are taken from the original sample and the second one after further adding tetrabutylamonium chloride. The 480 nm profile shows the corresponding delayed formation of aminyl radicals.

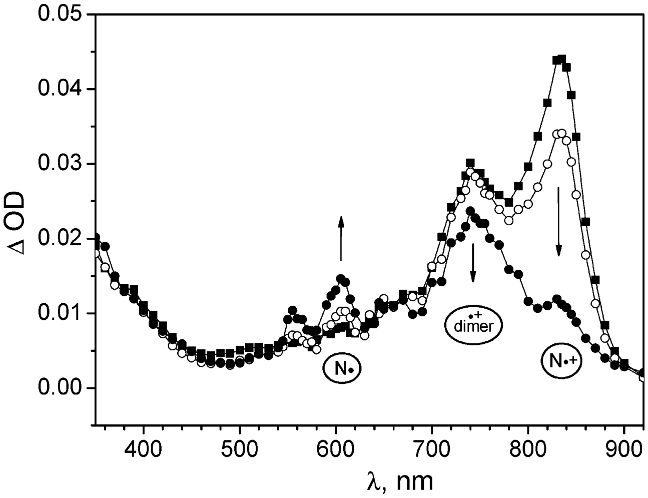


Figure 4. Transient spectra obtained in the pulse radiolysis of a solution of 10^{-3} mol dm^{-3} carbazole in *n*-butyl chloride: (■) 150 ns, (○) 330 ns, and (●) 1.9 μs after the pulse.

From the experimental side, in the FET with acridane dominantly amine radical cations are generated, and only a very minor part of the directly formed aminyl radicals appears.

Pulse Radiolysis of Carbazole Samples. In FET, the completely planar carbazole molecule shows primarily only the formation of amine radical cations. Figure 4 gives absorption spectra taken at different times after the electron pulse from a solution of 1×10^{-3} mol dm^{-3} carbazole in *n*-butyl chloride. Immediately after the pulse and after the decay of the $\text{BuCl}^{\bullet+}$ signal (after 150 ns) a dominating absorption with $\lambda_{max} = 840$ nm and a shoulder type maximum at $\lambda_{max} = 750$ nm are observed. Furthermore, below 400 nm less specific signals exist. Through the increase of the concentration of carbazole, the 750 nm absorption increases considerably on costs of the 840 nm signal. Both species seem to be of ionic origin. In analogy to similar planar aromatic systems (see acridane), we assign the 840 nm species to the carbazole radical cation and the 750 nm absorption to the corresponding charge-transfer dimer cation; cf. eq 4.

At longer times and concomitant with the decay of both types of the amine radical cations, around 600 nm a two-peak absorption appears which is characteristic for the carbazole aminyl radical. But this absorption clearly did not exist from the very beginning, that is, it is not a direct product of the electron transfer analogous to 2. As shown in Figure 5, by

TABLE 1: Experimental and Calculated Optical Absorption Maxima of the Transients Derived from the Cyclic Aromatic Amines

	λmax (nm)	acridane	carbazole	phenothiazine
c-$Ar_2NH^{\bullet+}$	λ_{exp}	680,[a] 650(16) broad band	840,[a] *810*, 725(17)	520[a], 437, *515*,(18) 440, *530*(19)
radical cation	$\lambda_{calc}{}^{a}$	570 (0.18), 630 (0.03)	772 (0.11)	483 (0.15), 492 (0.02)
(c-$Ar_2NH)_2{}^{\bullet+}$	λ_{exp}	640[a]	750[a]	not found[b]
dimer radical cation (CT complex)	$\lambda_{calc}{}^{a}$	618 (0.148), 1633 (0.124)	873 (0.075), 1498 (0.014), 1595 (0.072)	492 (0.014), 2045 (0.131)
c-$Ar_2N^{\bullet}$	λ_{exp}	350,[a] 510[a]	555,[a] 605,[a] 560, 620(20−22)	435,[a] 520[a]
aminyl radical	$\lambda_{calc}{}^{a}$	355 (0.028), 454 (0.058)	534 (0.086), 627 (0.001), 934 (0.086)	408 (0.022), 550 (0.013)

[a] This paper,(xx) literature data. [b] If existent, then very superimposed with the aminyl radical absorption.

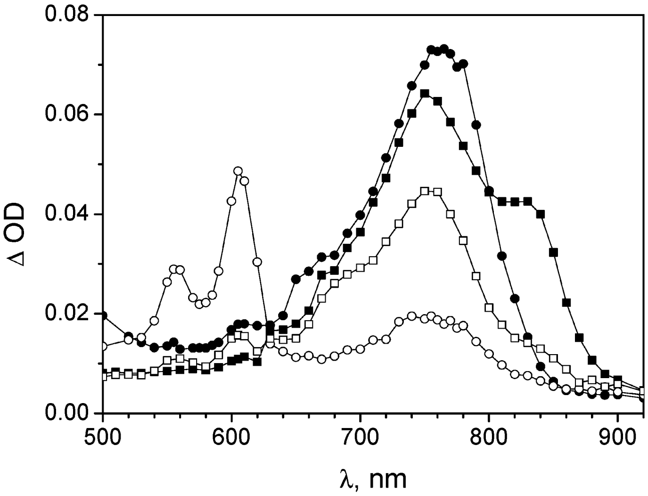


Figure 5. Transient spectra obtained in the pulse radiolysis of 10^{-2} mol dm^{-3} carbazole in deaerated *n*-butyl chloride taken (■) 40 ns and (□) 1.8 μs after the pulse. Further spectra are obtained in the same solution after the addition of 0.1 mol dm^{-3} DMSO (●) 40 ns and (○) 1.8 μs after the pulse.

increasing the carbazole concentration up to 10^{-2} mol dm^{-3} and adding 0.1 mol dm^{-3} DMSO, we could demonstrate (i) the domination of the dimer cation (see above, reaction 4) and (ii) the quenching of the cationic species by the polar additive DMSO under aminyl radical formation. The latter point is also direct proof for the statement that in FET with carbazole only cationic species of the amine are formed.

Discussion

Identification of the Amine Transients. The knowledge about spectral and kinetic properties of the radical cations of the secondary cyclic amines studied in this paper is very limited. It originates mainly from low-temperature, steady-state, γ irradiation experiments performed by Shida et al. (acridane,[16] carbazol[17]) in glassy *sec*-butyl chloride. Under those conditions, the radical cations are characterized in frozen solution where no dimerization (4) is expected to happen. For liquid solutions of phenothiazine some hints on radical cation spectra exist after solving phenothiazine in concentrated sulfuric acid[18] and from laser flash photolysis work in micellar solution.[19]

The corresponding aminyl radicals of the cyclic aromatic amines were produced by photodeprotonation,[20] by abstraction with peroxyl radicals,[21] or by photolysis of hydrazines.[22] The data of these species are compared with our experimental results in Table 1.

Because we possessed such a set of experimental data, it was tempting to perform quantum chemical spectra calculations using an unrestricted time-dependent DFT program.[15] The obtained data are also added to the experimental ones in Table 1. Surprisingly, a very high agreement of the spectral maximum values is observed. In each case, the energetic correlation of the optical spectra bands is given.

Because some of the literature data are not so convincing, some considerations about the identification of the species should be made. The species generated in FET are clearly of ionic origin. Certainly, as primary products of this reaction the amine radical cations and in some cases aminyl radicals are observed, cf. Scheme 1. As secondary products, however, the amine dimer cations (cf. reaction 4) and a further part of the aminyl radicals is formed (cf. reaction 3). Both cation types can be distinguished by their lifetime and by their reactivity against the nucleophile Cl^-. As observed in similar cases,[6,23] the monomer and the dimer radical cations of the aromatic amines are less sensitive against oxygen. But also the aromatic aminyl radicals exhibit minor sensitivity against oxygen. They decay by recombination (6).

$$2\ \text{c-}Ar_2N^{\bullet} \rightarrow \text{c-}Ar_2N{-}NAr_2\text{-c} \qquad (6)$$

A characteristic identification and transformation path is given by the addition of DMSO. Then a stepwise electron transfer (7) happens followed by an efficient deprotonation (8) of both types of amine radical cations forming aminyl radicals. This can be seen well on the example of the carbazole cations (Figure 5). Here, the aminyl radicals exhibit a very marked two-band absorption around 600 nm. The intermediate DMSO radical cation has an absorption maximum around 400 nm (not shown here).

$$BuCl^{\bullet+} + DMSO \rightarrow BuCl + DMSO^{\bullet+} \qquad (7a)$$

$$DMSO^{\bullet+} + \text{c-}Ar_2NH \rightarrow \text{c-}Ar_2NH^{\bullet+} + DMSO \qquad (7b)$$

$$\text{c-}Ar_2NH^{\bullet+} + DMSO \rightarrow \text{c-}Ar_2N^{\bullet} + H^+(DMSO) \qquad (8)$$

Now the peculiar situation of the free electron transfer in the presence of the cylic aromatic amines should be analyzed.

Properties of FET. Some of the properties of FET were already mentioned in the Introduction. One crucial point is that the gross reaction of the electron transfer should be analyzed in terms of its single steps:

(i) The diffusional approach of the reactants is the slowest step taking place in a few tens of nanoseconds, depending on the scavenger concentration. It governs the rate constant of the FET which for the case of the cyclic aromatic amines was found to be about $k_2 = (1.5-2.0) \times 10^{10}$ dm^3 mol^{-1} s^{-1}.

(ii) Then the real electron jump happens in extremely short times, that is, at the border between atto- and femtoseconds. One of the reasons for this is that in the nonpolar system the ions are practically not solvated. Therefore, after something like a collision of the reactants, the reaction takes place immediately

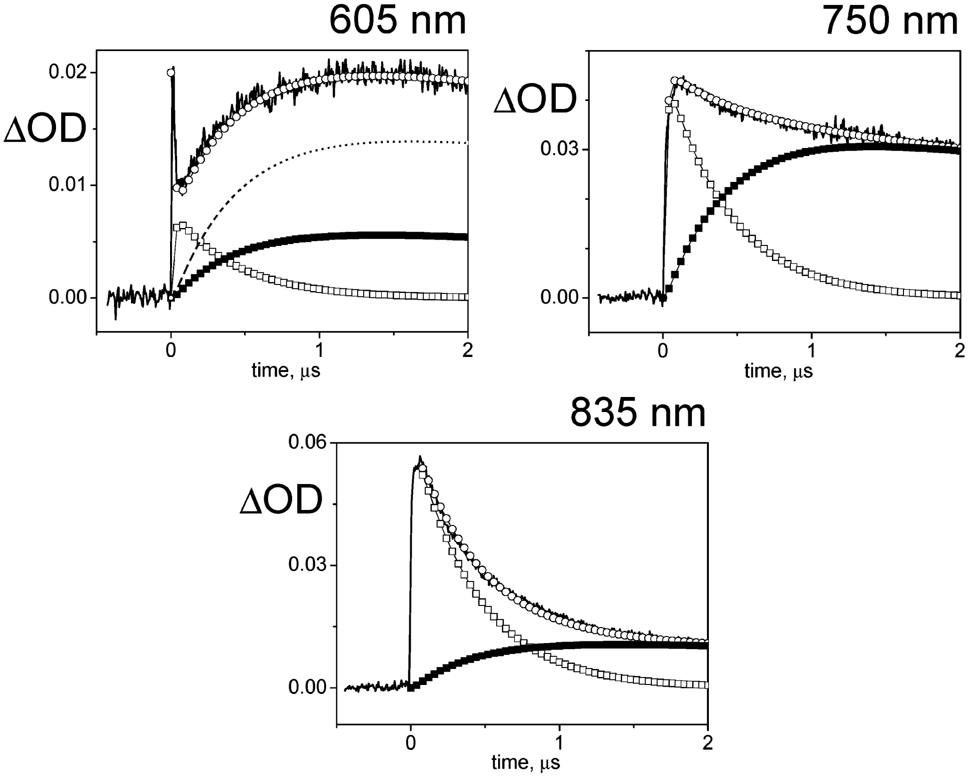


Figure 6. Simulation of experimental time profiles (—) resulting after pulsing a solution of 2 × 10^{-3} mol dm^{-3} carbazole in deaerated *n*-butyl chloride: (○) simulated time profile, (- - -) carbazole aminyl radical, (□) carbazole radical cation, and (■) carbazole dimer radical cation.

or repulsion again causes separation. Under those conditions no encounter complexes should exist.[6]

(iii) After the electron jump, the solvent parent ion is a repaired molecule and becomes anonymous. Excess energy is mainly distributed to the surroundings.

(iv) Concerning the products, the electron jump is much faster than any rotation or bending motions within the electron donor molecule. Therefore, the ionization takes place in each geometric constellation of the bending motions of the molecule, leading to a variety of conformer scavenger radical cations. Simplified to both extremes, two types of cations should be formed such as a stable mesomeric and planar type one as well as a cation localized at the heteroatom N (see Scheme 1).

(v) The stable and mesomeric cation relaxes and overcomes into the nanosecond time range whereas the localized one deprotonates immediately, certainly assisted by the solvent or the present nucleophile.

In the case where the product cations have such an extremely different stability, the very rapid electron jump can be visualized by the bimolecular electron transfer. This has been found already in a variety of cases[2−8] and has been reported recently for the example of the FET involving differently substituted anilines.[6]

Interpretation of the Electron-Transfer Data Involving Cyclic Amines. From the pulse radiolysis experiments elucidated above, it seems to be substantiated that for the cyclic aromatic amines with mobility restrictions only for the ionization of phenothiazine amine radical cations and aminyl radicals appear as direct products of FET. In contrast, for carbazole only radical cations were formed. Acridane follows in the main the example of carbazole, but it seems to form a very minor amount of primary aminyl radicals as well.

To demonstrate this interpretation ACUCHEM simulations[3] were performed and adapted to the time behavior of the optical absorption at different wavelengths. This is shown on the example of the time profiles given in Figures 2 and 6 for the cases of phenothiazine and carbazole as electron donors. For the simulations, a set of known rate constants of the involved reactions has been used with the only free parameter of the ratio (defined by the extinction coefficients) between both products of FET. The time profile sets given in Figures 2 and 6 stand for the two opposite reaction paths of FET. So Figure 2 demonstrates the formation of amine radical cations as well as aminyl radicals for the case of phenothiazine. Figure 6 shows, using carbazole as the example, how only the amine radical cations are primarily formed, which dimerize and subsequently decay by the reaction with the nucleophile Cl^-. Generally, the deprotonation was found to be independent of the amine concentration, that is, a self-deprotonation does not take place. The mentioned elementary reactions and the rate constants used for the fitting procedure are given subsequently in reaction sequence 9

$$\mathrm{BuCl}^{\bullet+} \rightarrow \text{self-decay} \tag{9a}$$

$$k_{9a} = 8 \times 10^{6}\ \mathrm{s}^{-1}$$

$$\mathrm{BuCl}^{\bullet+} + \mathrm{Ar_2NH_{planar}} \rightarrow \mathrm{BuCl} + [\mathrm{Ar_2NH}]^{\bullet+} \tag{9b}$$

$$k_{9b} = 1.5 \times 10^{10}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$$

$$\mathrm{BuCl}^{\bullet+} + \mathrm{Ar_2NH_{twisted}} \rightarrow [\mathrm{Ar_2N^{\bullet+}H}] \rightarrow \mathrm{Ar_2N}^{\bullet} + \mathrm{H^+(BuCl)} \tag{9c}$$

$$k_{9c} = k_{9b}$$

$$[\mathrm{Ar_2NH}]^{\bullet+} + \mathrm{Cl}^- \rightarrow \mathrm{Ar_2N}^{\bullet} + \mathrm{HCl} \tag{9d}$$

$$k_{9d} = 5 \times 10^{9}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$$

$$2\mathrm{Ar_2N}^{\bullet} \rightarrow \text{products} \tag{9e}$$

$$k_{9e} = 2 \times 10^{9}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$$

TABLE 2: Results of the Quantum-chemical Calculation [B3LYP/6-31G(d)] of Energetic and Dynamic Parameters for the Ground and for the Radical Cation State of the Cyclic Aromatic Amines Investigated in This Paper[a]

	singlet					radical cation					
	structure	ΔE, kJ/mol	ν_{bend} cm^{-1}	ν_{bend} ps	$Q(\mathrm{N})^b$	structure	ΔE, kJ/mol	$Q(\mathrm{N})^b$	$P(\mathrm{N})^b$	$P(\mathrm{S})^b$	E_{st} kJ/mol^c
acridane	nonplanar	0.0	44	0.76	−0.470	nonplanar	+19.2	−0.316	0.373		47
	planar	+1.3			−0.526	planar	0.0	−0.383	0.348		
phenothiazine	nonplanar	0.0	55	0.61	−0.415	nonplanar	+32.2	0.301	0.274	0.260	48
	planar	+7.0			−0.491	planar	0.0	−0.375	0.256	0.273	
carbazol	planar				−0.490	planar		−0.350	0.318		75

[a] Frequencies ν (cm^{-1})and period τ (ns) of the lowest out-of-plane bending motion for molecules c-Ar$_2$NH in their ground-state singlet and relative energy ΔE of planar and nonplanar structures. [b] Q(N), P(N), and P(S) are Mulliken atomic charge and spin density on N and S atoms, respectively, in dependence on molecular geometry. [c] Stabilization energy E_{st} of the dimer radical cation.

For carbazole and acridane

$$[\mathrm{Ar_2NH}]^{\bullet+} + \mathrm{Ar_2NH} \rightarrow (\mathrm{Ar_2NH})_2^{\bullet+} \qquad (9f)$$

$$k_{9f} = 7 \times 10^8\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$$

$$(\mathrm{Ar_2NH})_2^{\bullet+} \rightarrow [\mathrm{Ar_2NH}]^{\bullet+} + \mathrm{Ar_2NH} \qquad (9g)$$

$$k_{9g} = 2 \times 10^5\ \mathrm{s^{-1}}$$

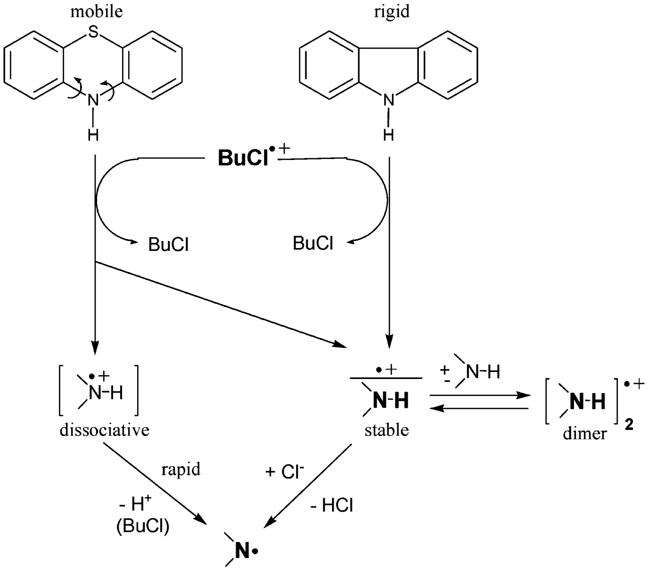
In accordance with the experimental findings, for carbazole a simple simulation assuming amine radical cations as the only direct FET product and its decay by the dimerization equilibrium and the subsequent reaction with the nucleophile Cl$^-$ gave a sufficient result; cf. profiles of Figure 6.

For phenothiazine, however, the rapid and the delayed part of the aminyl radical could be demonstrated well (Figure 2). Here no dimerization has been found which could be understood considering the longer distances of CT interaction in the case of the deformed systems. However, a little and hidden dimer absorption covered by the radical absorption would not influence the mechanism markedly. For this substance, the stable ground state configuration is out-of-plane. The ratio between both products of FET is about 1:1 which was roughly estimated from the simulations (relation between rapid and delayed formation of the aminyl radicals).

Quantum Chemical Calculations on the Geometry, Electron Distribution, and Dynamics. What remains is answering the question for the stability or instability of the intermediate amine radical cations. As something like an exception, in a cyclic aromatic amine molecule containing sulfur (such as phenothiazine) a distinct bending motion seems to be given.

For a better understanding of the experimental results, we performed quantum chemical calculations on singlet and radical cation parameters using the B3LYP/6-31G(d) method. Table 2 gives data on the different conformer extremes. It shows that phenothiazine attracts special attention because here for the singlet and more pronounced for radical cation state the relative stablilization energy differences ΔE between the planar and the nonplanar state are the highest when compared with the other amines. Clearly, (in the ground state) the nonplanar configuration is the stable one. Furthermore, the spin density of the phenothiazine radical cation is distributed to N and S atoms nearly to the same amount, that is, the charge is more delocalized as for the cases of acridane and carbazole cations. Although the stabilization energy of the dimer radical cation of acridane and phenothiazine is comparable, no phenothiazine dimer cation has been observed experimentally. Either it is covered by the other products or more probable it does not exist because of the efficient delocalization of the charge. For the rigid planar molecule carbazole, the dimer cation stabilization energy is the highest indicating that the distance between the partners is the smallest.

SCHEME 2: Transient Transformations for Cyclic Diphenylamine Derivatives



For the flexible phenothiazine ground-state molecule, the frequency of the bending motion of the >NH group amounts to about 1.6 × 10^9 Hz which corresponds to 0.6 ps per cycle. Excluded for carbazole and comparable for acridane, for these molecules, the amplitude of the bending motion is negligible; see also the ΔE values. Overall, the data demonstrate a correlation with the experimental results which mainly means that the two conformer radical cations and their subsequent products (radical cation and radical) for the case of phenothiazine are motivated. This is also in agreement with the former findings that aniline, 1-methylaniline, and diphenylamine show in FET the two products (radical cation and aminyl radical). Here the mechanism of the extremely rapid deprotonation of the unstable amine radical cation of phenotiazine should be mentioned. As also in the case of the mobile aniline-type molecules,[6] the deprotonation happens in interaction with the solvent (9c). The high energy difference between both borderline conformer states of the amine radical cation ($\Delta E = 32$ kJ mol^{-1}; see Table 2) indicates that the proton affinity of the unstable conformer cation is much less than that of the stable one and, therefore, it would approach the proton affinity of the solvent. If so, the deprotonation happens immediately after cation formation, that is, in the femtosecond time scale. Certainly, vibrational and structural relaxation should also play a role. For the lack of defined knowledge about it we state that dissociation is efficiently competing with these relaxation processes.

Furthermore, and that is the main point of the paper, the rigid molecule structures of the cyclic secondary amines carbazole and acridane generate in the FET ionization exclusively radical cations. This confirms the hypotheses that the product distribution in FET is mainly governed by the molecular dynamics of the electron donor molecules which takes place in the femtosecond time range.

This interpretation of the free electron transfer events involving the cyclic aromatic amines is concluded in reaction Scheme 2. The left side (phenothiazine) describes the two-product situation for the flexible aminyl group whereas the right-hand side shows simple electron transfer involving a rigid amine structure (carbazole) forming amine radical cations only. In the scheme, the directly observed transients are printed in boldfaced manner. This shows that the discussion is based on a fully consistent set of data.

Conclusions

The combination of experimental results with quantum chemically calculated data on the molecular dynamics given in this paper supports strongly the hypotheses about the mechanism of free electron transfer in nonpolar liquids. If allowed by molecule flexibility, the bending motion of the amine functionality of the cyclic aromatic amines is accompanied with fluctuation of the highest occupied molecular orbital electrons (or that of n-orbitals). So, a standing mixture of something like molecule conformers is reasoned. In FET, this conformer mixture generates principally two cation types of different spin localization which also differ in their stability. This rationalizes the two mentioned products (radical cation and radical) in the flexible systems or only one (amine radical cation) if the bending motion is strongly restricted or impossible. So, the efficient electron jump as part of the gross FET reaction is a rapid electron transfer which reflects the femtosecond dynamics of the donor molecule, that is, it is something like a bimolecular femtochemistry event.

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