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Quenching of n,π*-excited azoalkanes by amines: structural and electronic effects on charge transfer

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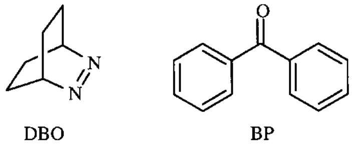
ABSTRACT: The quenching of n,π* singlet-excited 2,3-diazabicyclo[2.2.2]oct-2-ene, a very weak electron acceptor, by 26 aliphatic and aromatic amines was investigated in benzene. This photoreaction entails fluorescence quenching through exciplex formation with subsequent hydrogen atom abstraction from the N—H and α C—H bonds of the amines (photoreduction). The quenching rate constants for aliphatic amines lie in the range 10^7–10^9 M^{-1} s^{-1}, while those for the aromatic amines are generally higher and reach the diffusion-controlled limit in some cases, e.g. 7.3×10^9 M^{-1} s^{-1} for *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine. A dependence of the magnitude of the fluorescence quenching rate constant on the adiabatic ionization potential reveals significant scatter. Besides steric and stereoelectronic effects, variations in the dissociation energies of the C—H and N—H bonds of the amines appear to be responsible for the deviations, e.g., the faster quenching of secondary amines compared with primary amines is presumably related to the weaker secondary N—H bond dissociation energy. Solvent effects, deuterium isotope effects, and photoreaction quantum yields were determined. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: n,π*-excited states; quenching; amines; charge transfer

INTRODUCTION

The mechanistic understanding of the transfer of electrons, protons and hydrogen atoms is of great importance since many photochemical and photobiological processes are based on these primary events. The quenching of n,π*-excited ketones and azoalkanes by amines which usually leads to the formation of photoreduction products is a prototypical reaction in this respect. While a ‘direct’ hydrogen abstraction competes in some cases,[1] the dominant photochemical process is assumed to involve electron transfer in the case of ketones.[2–4] The primary radical ion pair may undergo proton transfer or back electron transfer which results in an overall hydrogen transfer or deactivation, respectively. In support of this mechanism, quenching rate constants generally increase with decreasing ionization potential of the quencher and increasing solvent polarity unless specific solvation,[3,5,6] steric[4] or stereoelectronic effects[7,8] operate.

Alternatively, the involvement of excited charge-transfer complexes or exciplexes, i.e. intermediates with partial charge-transfer character, has been suggested in the quenching of n,π*-excited ketones and azoalkanes by amines.[3,7,9–12] Since direct spectroscopic detection through exciplex emission has not been achieved, reduced quantum yields[11,13], small or ‘inverted’ solvent effects,[9,12,14] steric hindrance effects[15], a low sensitivity of the quenching rate constants on the donor propensity of the quencher,[9] and related observations for olefins and aromatic quenchers[16–21] have been taken as indirect experimental indications for exciplexes.



The azoalkane 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO) represents an n,π* chromophore with novel, interesting properties. These include an exceedingly long singlet lifetime (up to 1 μs in the gas phase)[22] and a low-lying reduction potential ($E_\text{p} = -2.8$ V vs SCE).[12] The latter renders DBO a very weak electron acceptor, for example, much weaker than triplet-excited benzophenone (BP). For such weak acceptors quenching occurs below the diffusion-controlled limit,[4,23] which allows further insights into structure–reactivity relationships to be gained. Since steric and stereoelectronic effects have already been discussed[15], the present study was focused on structural and electronic variations of the amine quenchers, e.g. their alkylation pattern and their donor strength.

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EXPERIMENTAL

Materials. DBO was synthesized according to the literature.[24] All amines are commercially available (Aldrich or Fluka) and some were further purified before use by distillation (**11, 21**), recrystallization (**16, 24, 25**) or sublimation (**18**). Benzene (Merck, Uvasol), acetonitrile (Scharlau, Multisolvent grade), *n*-hexane (Scharlau) and cyclohexane (spectroscopic grade, Fluka) were used as received. D_2O (>99.9%) was purchased from Glaser (Basel, Switzerland) All measurements were performed at ambient temperature (24 °C).

Methods. Samples were prepared by dissolving the azoalkane (ca 0.1–1 mM) and the appropriate amounts of the amine were added with a GC syringe, either neat or as a stock solution. The samples were deaerated by three freeze–pump–thaw cycles. Experimental details of the time-resolved fluorescence measurements were described previously.[25] The quantum yield for the reaction of DBO in the presence of amines was determined as described previously.[25] The decomposition quantum yield of DBO in the particular solvent (3.3, 2.3, 0.1 and 1.3% in cyclohexane *n*-heptane, benzene, water and acetonitrile) (M. P. Feth, G. Greiner, H. Rau and W. M. Nau, Unpublished results), was employed for actinometry.

RESULTS

Laser excitation of DBO in deaerated benzene (351 nm, FWMH ≈ 20 ns) populates the strongly fluorescent singlet state (λ_{max} = 430 nm, singlet energy ca 318 kJ mol^{-1}),[22] which has a lifetime of 490 ns in the absence of quencher (τ_0). Successive addition of an amine decreased the fluorescence lifetime (τ_q). Kinetic plots according to Eqn. (1) were linear in each case (4–6 data points) and the slopes afforded the bimolecular quenching rate constants (Tables 1 and 2):

$$\tau_0/\tau_q = 1 + \tau_0 k_q[\text{amine}] \qquad (1)$$

Thermodynamics of electron transfer

The driving force (ΔG_{et}) for photoinduced electron transfer can be estimated according to Rehm and Weller [Eqn. (2)][23] with the oxidation potential of the donor, $E_{ox}(D)$, the reduction potential of the acceptor, $E_{red}(A)$, and the excitation energy of the acceptor, E^*. C is the coulomb term which entails the electrostatic interaction within the radical ion pair. This term is solvent dependent and has a value of −0.06 eV for acetonitrile. The calculated ΔG_{et} values for some limiting cases are provided in Table 3. Only for the strongest aromatic donors, e.g. amines **18** and **19**, is electron transfer to DBO expected to be slightly exergonic. All other amines give positive values for ΔG_{et}. The thermodynamics for triplet-excited benzophenone (BP), shown for comparison, is exergonic even for the weak donors.

$$\Delta G_{et} = E_{ox}(D) - E_{red}(A) - E^* + C \qquad (2)$$

Most amines used in this study show irreversible oxidation in cyclovoltammetry owing to the fast follow-up reactions of the resulting aminyl radical cations, mostly deprotonation.[39] Since the use of Eqn. (2) requires reversible potentials, the values in Table 3 are conservative estimates. As an alternative, more consistent parameter than irreversible oxidation potentials the adiabatic ionization potentials (IP_a) of the amines are used throughout this work to characterize trends of the donor strength (Tables 1 and 2). These gas-phase data and the electrochemical oxidation potentials measured in solution are correlated.[38,40]

Quenching rate constants

In previous studies, aromatic amines were discussed separately from aliphatic amines.[10,41] The former may also donate electrons from their aromatic rings ('π-donors'), while the latter act as pure 'n-donors.' For this reason these two donor classes are grouped together in Tables 1 and 2, although, as will be seen below, such a separation is not required on the basis of the present results.

Among the *aliphatic* amines, the quenching rate constants (k_q) lie in the range 10^7–10^9 M^{-1} s^{-1} (Table 1). Especially for primary and tertiary amines the rate constants fall far below the diffusion-controlled limit (ca 10^{10} M^{-1} s^{-1} in benzene). Primary amines are the poorest quenchers, while secondary amines quench DBO most efficiently ($k_q \approx 10^9$ M^{-1} s^{-1}). This confirms the general trend: secondary > tertiary > primary. For the *aromatic* amines, fluorescence quenching is generally fast and approaches the diffusion-controlled limit in some cases. The reactivity trend observed for the aliphatic amines, namely secondary > tertiary, is obtained also for the aromatic derivatives. Surprisingly, however, the quenching rate constant of the primary aromatic amine aniline (**26**) falls into the range (3.1×10^9 M^{-1} s^{-1}) of the secondary aromatic amines.

Except for the secondary amines k_q generally increases with decreasing IP_a of the amine. This approximate relationship is shown for the aliphatic amines in Fig. 1 and for the aromatic amines in Fig. 2 (solid data points). However, there is significant scatter especially in Fig. 1: although the primary amines cyclohexylamine (**1**) and *tert*-butylamine (**2**) have the same ionization potential, amine **1** quenches DBO three times as fast. Even among the tertiary amines some inconsistencies are found: tri-*n*-propylamine (**13**) and *N*-ethyldiisopropylamine (**14**) have similar donor strengths but amine **14** has a two times higher quenching rate constant.

Table 1. Quenching of DBO by aliphatic amines in benzene

No.	Amine	IP_a/eV[a]	$k_q/(10^8\ M^{-1}s^{-1})$[b]	
			^{1}DBO*	^{3}BP*
Primary amines				
1	Cyclohexylamine	8.62	0.27	3.3[c]
2	*tert*-Butylamine	8.64	0.082	0.64[c]
3	Benzylamine	8.64	0.42	
4	*sec*-Butylamine	8.70	0.21	2.3[c]
5	*n*-Butylamine	8.71	0.28	
Secondary amines				
6	2,2,6,6-Tetramethylpiperidine	7.59[d]	4	21[e]
7	Di-*n*-butylamine	7.69[f]	12	
8	Diisopropylamine	7.73[f]	3.9	
9	Di-*n*-propylamine	7.84[f]	11	34[c]
10	Diethylamine	8.01[f]	12	
Tertiary amines				
11	*N*-Ethyldicyclohexylamine	6.85[g]	2.5[h]	45[g]
12	Tri-*n*-butylamine	7.15	0.92[i]	35[j]
13	Tri-*n*-propylamine	7.18	0.85[i]	
14	*N*-Ethyldiisopropylamine	7.20[g]	1.3[h]	47[g]
15	1,2,2,6,6-Pentamethylpiperidine	7.23[d]	0.89[h]	34[e]
16	Tribenzylamine	7.35[k]	0.58	
17	Triethylamine	7.50	0.72[i]	17[l]

[a] Adiabatic ionization potentials from Ref. 26.
[b] Measured with time-resolved fluorescence spectroscopy; error in data is 5–10%.
[c] Ref. 3.
[d] Ref. 27.
[e] Ref. 28.
[f] Ref. 29.
[g] Ref. 4; in acetonitrile.
[h] Ref. 15.
[i] Ref. 12.
[j] Ref. 10.
[k] Estimated from the vertical ionization potential[30] by subtraction of 0.7 eV.
[l] Ref. 31.

Table 2. Quenching of DBO by aromatic amines in benzene

No.	Amine	IP_a(eV)[a]	$k_q(10^8\ \mathrm{M}^{-1}\ s^{-1})$[b]	
			^{1}DBO*	^{3}BP*
18	*N*,*N*,*N*′,*N*′-Tetramethyl-*p*-phenylenediamine	6.20[c]	73	
19	*N*,*N*,*N*′,*N*′-Tetramethyl-1,8-naphthalenediamine	6.45[d]	25	
20	Triphenylamine	6.86[e]	2.1[f]	7.6[g]
21	*p*-Methyl-*N*,*N*-dimethylaniline	6.95[c]	5.3	43[h]
22	*N*,*N*-Dimethylaniline	7.12[c]	2.4[f]	27[h]
23	*N*,*N*-Diphenylamine	7.16[c]	52	130[i]
24	Carbazole	7.57[j]	48	
25	*p*-Cyano-*N*,*N*-dimethylaniline	7.60[k]	0.78	20[h]
26	Aniline	7.72[c]	31	

[a] Adiabatic ionization potentials.
[b] Measured with time-resolved fluorescence spectroscopy; error in data is 5–10%.
[c] Ref. 26.
[d] Ref. 32.
[e] Ref. 29.
[f] Ref. 12.
[g] Ref. 33.
[h] Ref. 34.
[i] Ref. 1; in isooctane.
[j] Ref. 35.
[k] Estimated from Ref. 36.

Table 3. Thermodynamics of photoinduced electron transfer

No.	Amine	E_{ox} vs SCE (V)[a]	ΔG_{et} (eV)[b] ^{1}DBO*	^{3}BP*
11	*N*-Ethyldicyclohexylamine	0.61[c]	+0.05	−0.62
13	Tri-*n*-propylamine	0.71[c]	+0.15	−0.52
18	*N*,*N*,*N'*,*N'*-Tetramethyl-*p*-phenylenediamine	0.13[d]	−0.43	−1.10
19	*N*,*N*,*N'*,*N'*-Tetramethyl-1,8-naphthalenediamine	0.36[e]	−0.20	−0.87
20	Triphenylamine	0.85[f]	+0.29	−0.38
21	*p*-Methyl-*N*,*N*-dimethylaniline	0.72[d]	+0.16	−0.51

[a] Oxidation potential of the amine; E_p for **11, 13, 19**; $E_{p/2}$ for **18, 20, 21**; in acetonitrile.
[b] Driving force; estimated according to Eqn. (2) with E_{red} (DBO) = −2.8 V[12] and E_{red} (BP) = −1.83 V[18] *vs* SCE in acetonitrile, E^* = 3.3 eV for DBO[12] and 3.0 eV for BP [18], C = −0.06 eV in acetonitrile.
[c] Ref. 15.
[d] Ref. 38.
[e] Ref. 37.
[f] Ref. 11.

The quenching rate constants for triplet benzophenone (BP) are included in Tables 1 and 2 to illustrate the diffusion-controlled nature of the quenching of this excited ketone by most amines. Structural or electronic effects are difficult to recognize for this ketone and this unfortunate situation originally motivated our study of the less reactive, more selective azoalkane DBO.

It should be noted that perfluorotriethylamine was also examined as an extreme case of an amine with an exceedingly high ionization potential (IP_v = 12.0)[42] and the fluorescence lifetime was 590 ns in the *neat* amine. Comparison with the lifetime in perfluorohexane (τ_0 = 605 ns)[22] demonstrates that this amine does not quench the fluorescence of DBO at all.

Deuterium isotope effects

Deuterium isotope effects were investigated for both N—H and C—H bonds (Table 4). For the primary amine *tert*-butylamine (**2**) and the secondary amine di-*n*-propylamine (**9**), significant N—H/N—D isotope effects were found, i.e. the quenching rate constants were lower for the deuterated amine and most pronounced for amine **2** (factor of 5 difference). For triethylamine (**17**) and its perdeuterated derivative a significant C—H/C—D isotope effect of 1.8 was also observed (*cf.* kinetic plots in Fig. 3).

Quantum yields

The reaction quantum yields shown in Table 5 are generally low (Φ_r < 5%) and follow the previously observed trend, i.e., tertiary ≈ primary > secondary amine, or **17** ≈ **5** > **10**.[11,13] Interestingly, the quantum yield decreases with increasing solvent polarity, i.e. cyclohexane ≈ benzene > acetonitrile > water (Table 5). This trend may be due to the intervention of exciplexes,

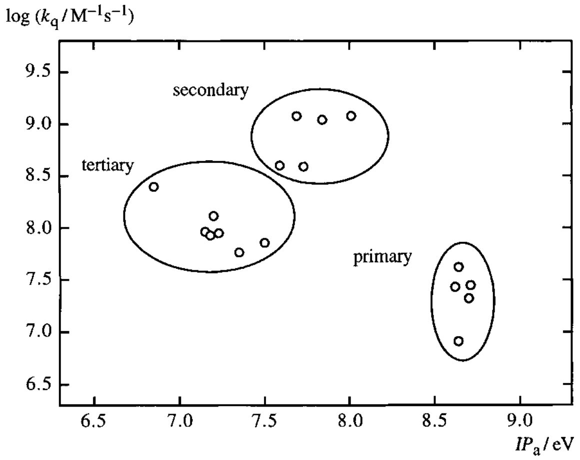


Figure 1. Plot of log k_q *vs* IP_a for the fluorescence quenching of DBO by the aliphatic amines in Table 1

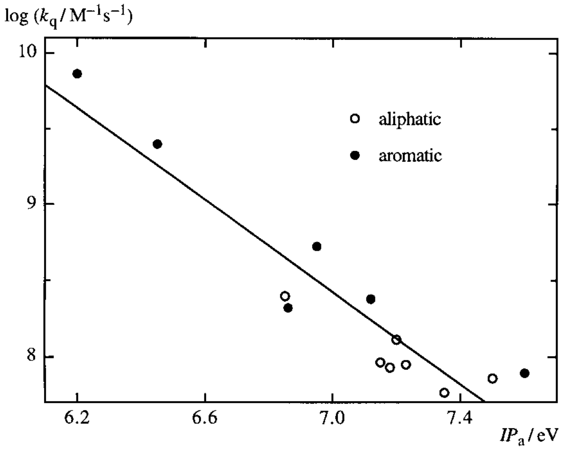


Figure 2. Plot of log k_q *vs* IP_a for the fluorescence quenching of DBO by the tertiary aliphatic and aromatic amines in Tables 1 and 2

Table 4. Deuterium isotope effects on the quenching of DBO by amines

No.	Amine	Solvent	k_q (10^7 M^{-1} s^{-1})[a]	k_H/k_D
2	*tert*-BuNH_2	H_2O	0.51	5.1
	tert-BuND_2	D_2O	0.1	
9	(n-Pr)$_2$NH	Acetonitrile[b]	14	1.8
	(n-Pr)$_2$ND		7.6	
17	$(C_2H_5)_3N$	Benzene	7.2	1.8
	$(C_2D_5)_3N$		4.0	

[a] Measured with time-resolved fluorescence spectroscopy; error in data is 5–10%.
[b] Containing 10% H_2O or D_2O as co-solvent, respectively.

Table 5. Reaction quantum yields for aliphatic amines in solvents of different polarity

No.	Amine	Solvent	Φ_r[a]
5	n-Butylamine	Benzene	0.045
10	Diethylamine	Benzene	0.020
17	Triethylamine	Benzene	0.044[b]
		Cyclohexane	0.038
		Acetonitrile	0.027[b]
		Water	0.006

[a] Excitation at $\lambda_{exc} > 345$ nm; error in data is 10%.
[b] Ref. 12.

since a 'direct' hydrogen abstraction should exhibit no dependence on the solvent.[43]

Solvent effects

We have recently found an 'inverted' solvent effect on the fluorescence quenching of DBO by triethylamine (**17**).[12] Additional amines were now also investigated in solvents of different polarity (hexane, benzene and acetonitrile) (Table 6). Except for *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (**18**), the inverted solvent effect was confirmed, i.e., the quenching rate constant decreased on going from the non-polar solvents hexane and benzene to the polar acetonitrile. Amine **18** showed a slight increase in reactivity upon changing from benzene to acetonitrile. Since this quencher reacts with the most exergonic thermodynamics (Table 3), a full electron transfer instead of exciplex formation may interfere. For such a scenario a normal solvent effect is expected.[12] However, no definitive conclusions can be drawn since the values lie close to the diffusion-controlled limit and for hexane a higher reactivity was again observed for amine **18**.

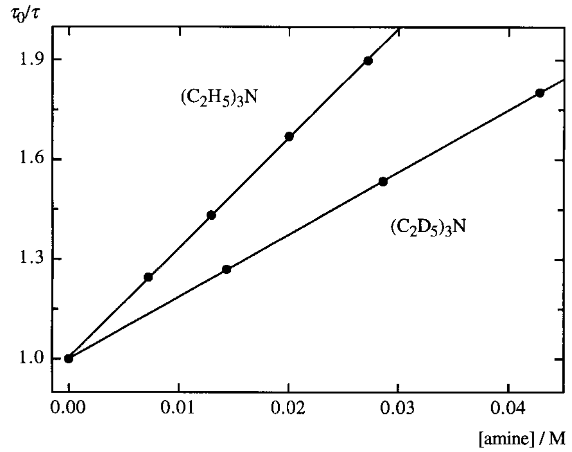


Figure 3. Kinetic plots according to Eqn. (1) for the fluorescence quenching of DBO by triethylamine (**17**) and its perdeuterated derivative

DISCUSSION

The photoreaction of n,π*-excited states by amines usually leads to the formation of the photoreduced chromophore and amine oxidation products.[11,13,43] This 'photoreduction' is known to be induced by an initial charge-transfer interaction between the reactants, with the amine as electron donor. While free ions may be formed in thermodynamically favorable cases (for strong acceptors), the formation of exciplexes becomes the presumed quenching pathway for weak acceptors,[44–46] e.g. for the azoalkane DBO, where free ions have not been detected in the quenching by amines.[47]

The observed photoreduction products of the azoalkanes (hydrazines)[13] and the low photoreaction quantum yields ($\Phi_r < 5\%$, Table 5) are diagnostic for a photoreaction, which involves a competition between exciplex-induced hydrogen abstraction from the α C—H or N—H bonds of the amines and exciplex-induced deactivation (Scheme 1).[11,13] The low rate constants for the quenching of DBO by amines (Tables 1 and 2) allow one to examine detailed structural and electronic effects of the donor compound on these reaction pathways. Previously, these effects have been difficult to analyze, e.g. for ketones such as benzophenone, where the quenching is virtually diffusion controlled (Tables 1 and 2).[4]

Quenching by primary amines

Primary aliphatic amines show the lowest rate constants as they have the highest ionization potentials. However, a significant variation of the quenching rates is noted, e.g. k_q(benzylamine) > k_q(cyclohexylamine) > k_q(*tert*-butylamine), although the ionization potential of the investigated primary aliphatic amines remains essentially constant. This behavior ('scatter') can be explained by the ease of α C—H hydrogen abstraction, i.e. the

Table 6. Solvent effects on the quenching of DBO by different amines

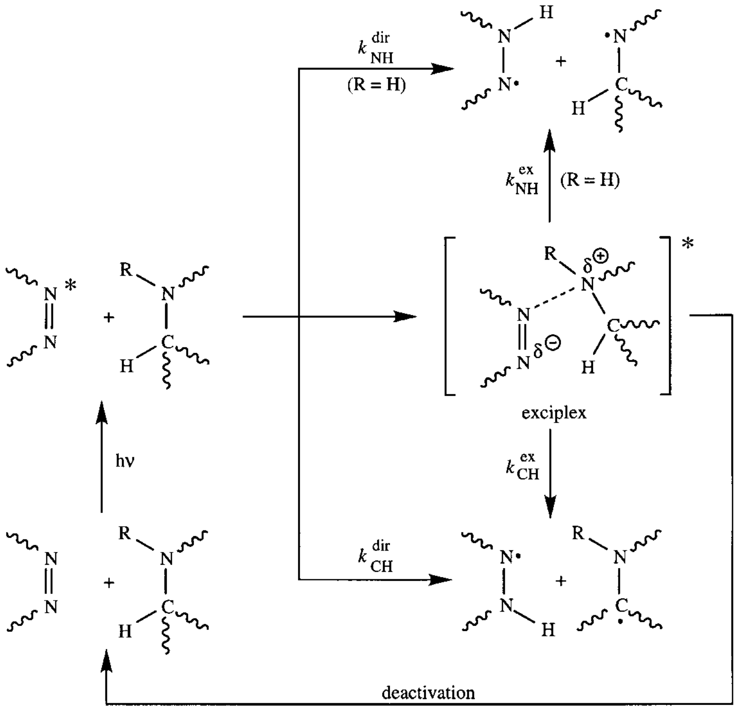
No.	Amine	k_q (10^8 M^{-1} s^{-1})[a] n-Hexane	Benzene	Acetonitrile
11	*N*-Ethyldicyclohexylamine	5.9	2.5	1.9
13	Tri-*n*-propylamine		0.85[b]	0.58
17	Triethylamine[b]	1.4[c]	0.72	0.44
18	*N*,*N*,*N*′,*N*′-Tetramethyl-*p*-phenylenediamine	130	73	95
20	Triphenylamine	4.3	2.1[b]	1.3
22	*N*,*N*-Dimethylaniline		2.4[b]	1.2

[a] Measured with time-resolved fluorescence spectroscopy; error in data is 5–10%.
[b] Ref. 12.
[c] Value in cyclohexane.

bond dissociation energy of the α C—H bonds ($BDE_{C—H}$). Hence benzylamine (**3**), which has particularly labile benzylic hydrogens available, is a better quencher than cyclohexylamine (**1**), and *tert*-butylamine (**2**), which has no abstractable α C—H hydrogens at all, is the poorest quencher. Similar arguments have been used previously to account for the scatter in the correlation of log k_q versus IP_a for the quenching of DBO derivatives by olefins.[21] While α C—H hydrogen abstraction is an important process for primary amines, it remains difficult to decide whether this hydrogen abstraction occurs directly (k_{CH}^{dir})or in an exciplex-mediated manner (k_{CH}^{ex}).[48]

Noteworthy is the large deuterium isotope effect which is observed for the quenching by *tert*-butylamine (**2**) ($k_H/k_D = 5.1$). This is the largest reported value for the quenching of an n,π*-excited state by an amine. For comparison, Inbar *et al.* observed a value of 1.8 for the benzophenone–*tert*-butylamine system.[3] The fact that our isotope effect approaches the theoretically predicted value of 7[49] corroborates the participation of N—H hydrogen abstraction in the quenching, i.e. k_{NH}^{dir} or k_{NH}^{ex} in Scheme 1.

The only primary aromatic amine investigated in the present study, aniline (**26**), has a larger quenching rate constant than expected from its adiabatic ionization potential. The underlying reason is the weaker N—H bond compared with aliphatic primary amines owing to aromatic delocalization (387 kJ mol^{-1} for aniline (**26**) versus 419 kJ mol^{-1} for methylamine).[50] Therefore ani-



Scheme 1

line (**26**) behaves more like a secondary amine, e.g. *N*,*N*-diphenylamine (**23**) and carbazole (**24**) (cf. Table 2).

Quenching by secondary amines

Based on the ionization potentials of the secondary aliphatic amines, one would expect the quenching rate constants to be between those of primary and tertiary aliphatic amines. However, the values lie near the diffusion-controlled limit and are the highest ones. The reason for this extraordinary behavior of the secondary aliphatic amines must be sought in competitive N—H hydrogen abstraction (k_{NH}^{dir}or k_{NH}^{ex}, Scheme 1). Indeed, the N—H bond energy for secondary amines ($402\ \text{kJ mol}^{-1}$) is significantly lower than for primary amines ($431\ \text{kJ mol}^{-1}$).[3] The measured deuterium isotope effect of 1.8 for di-*n*-propylamine (**9**) corroborates the involvement of the N—H hydrogens in the quenching. The smaller isotope effect compared with amine **2** ($k_H/k_D = 5.1$, Table 4) is presumably due to the higher quenching rate constant.

Interestingly, although the ionization potentials vary over a range of ca 0.3 eV for the secondary aliphatic amines, the quenching rate constants remain nearly constant except for 2,2,6,6-tetramethylpiperidine (**6**) and diisopropylamine (**8**). This insensitivity to the donor strength may indicate that the 'direct' hydrogen transfer pathway (k_{NH}^{dir})dominates.[1] The decrease of the quenching rate constant for the amines **6** and **8** may be due to the absence of abstractable α C—H hydrogens (amine **6**) or their unfavorable conformational arrangement (amine **8**).[15]

Quenching by tertiary amines

The tertiary aliphatic amines show the lowest ionization potentials among the aliphatic amines, i.e. they are the best electron donors. Amine **11** has the lowest ionization potential and, as expected, quenches DBO with the highest rate constant among the tertiary aliphatic amines. Noteworthy again is the scatter in the correlation with IP_a (Fig. 1). α C—H hydrogen abstraction, $k_{CH}^{dir}$and k_{CH}^{ex}in Scheme 1, may be one reason for this scatter. To test this hypothesis, fluorescence quenching experiments were carried out with triethylamine (**17**) and its perdeuterated derivative and a significant kinetic isotope effect of 1.8 was found. Similar but smaller effects (1.2–1.3) were reported by Inbar *et al.* for the quenching of benzophenone by *sec*-butylamine.[3] Based on the observation of an C—H/C—D isotope effect one expects the α C—H bond dissociation energy to be an important aspect for quenching. In line with this argument, *N*-ethyldiisopropylamine (**14**) is a better quencher than tri-*n*-propylamine (**13**), although both have nearly the same adiabatic ionization potential. This is expected since secondary C—H bonds are weaker than primary bonds.[51] The interpretation of the scatter for the tertiary aliphatic amines in terms of variations in the bond strength is not universal, however, since tribenzylamine (**16**) with its weak benzylic α C—H bonds quenches DBO unexpectedly slowly.

Quenching by aromatic amines

For the strongest aromatic donors, e.g. amines **18** and **19**, electron transfer may compete due to the exergonic thermodynamics (Table 3). Nevertheless, the quenching data can be treated in a similar way to those for the aliphatic donors, and an excellent correlation of log k_q with IP_a applies (Fig. 2). Especially the closely related *N*,*N*-dimethylaniline derivatives (including **19**), where the ionization potential can be fine-tuned through *para* substitution, show an accurately linear dependence ($r = 0.995$, $n = 5$). This provides additional, strong evidence for the involvement of charge transfer.

In previous studies of amine quenching, large variations in the reactivity of 'n-donors' (Table 1) and 'π-donors' (Table 2) were observed, a phenomenon which has been referred to as 'multiple Rehm–Weller plots'.[41,52] The 'π-donors' were found to be less reactive than 'n-donors' with the same donor strength. This was attributed to a charge localization for the aliphatic amines which results in a more negative Coulomb term and, thus, in a significantly higher reactivity according to Eqn. (2). In our study such a contrasting behavior was not observed, since tertiary 'n-donors' and 'π-donors' can be included in the same correlation (Fig. 2).[53] This supports an exciplex quenching mechanism,[41,44] where no free ions are formed and where the Coulomb term plays no role.

CONCLUSIONS

Structural effects of amines become particularly important when the quenching rate constants fall far below the diffusion-controlled limit as for the azoalkane examined here. The donor strength of an amine is one factor which governs the kinetics of fluorescence quenching of the azoalkane DBO. For tertiary aliphatic and aromatic amines, a correlation between the logarithmic quenching rate constants and the adiabatic amine ionization potential is observed. However, there is significant scatter in this correlation, which becomes more pronounced when primary and secondary amines are included. Unquestionably, the interplay between the donor strength of the amine, steric and stereoelectronic effects, and the bond strengths of both C—H and N—H is a complex one.[10,15,54] Trends become only apparent when a closely related series of amines is compared. The involvement of exciplexes of DBO and amines, i.e.

partial charge-transfer intermediates,[42] is suggested by the observation of an 'inverted' solvent effect,[12] low photoreaction quantum yields and the absence of 'multiple Rehm–Weller plots'.

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