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Interaction of triplet-excited benzophenone with hindered amines and amino ethers

A laser flash photolysis study employing photoconductivity and light emission measurements

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Abstract

Hindered amines such as 2,2,6,6-tetramethyl piperidines and *N*-methyl-2,2,6,6-tetramethyl piperidines and hindered amino ethers such as *N*-methoxy-2,2,6,6-tetramethyl piperidines were examined with respect to their reactivity towards triplet-excited benzophenone ($^3BP^*$) in Ar-saturated acetonitrile solution at room temperature. Upon measuring phosphorescence decay rates in the absence and presence of quencher it was found that the amines are two to three orders of magnitude more reactive than the amino ethers. For all amine/BP systems examined the generation of free ions was inferred from an increase in the electrical conductivity. This indicates that a charge transfer (CT) mechanism is operative in these cases. Notably, tertiary amines were found to be more reactive towards $^3BP^*$ and give higher free ion yields than secondary amines. In the case of amino ether/BP systems evidence for a CT mechanism was not obtained in spite of an increase in the electrical conductivity indicating the generation of free ions. The latter are formed much faster than the phosphorescence decays and very likely originate from triplet–triplet annihilation ($^3BP^* + {}^3BP^* \rightarrow BP^{\bullet +} + BP^{\bullet -}$). ©2000 Elsevier Science S.A. All rights reserved.

Keywords: Benzophenone; Hindered amines; Hindered amino ethers; Photoreactions

1. Introduction

The photoreduction of benzophenone (BP) by amines has been studied by many researchers [1–26]. Since intersystem crossing, $S_1 \rightarrow T_1$, is a very rapid process in the case of BP ($k \approx 10^{11}$ s^{-1}, [6,20]) the photoreduction in dilute solutions involves triplet excited benzophenone, $^3BP^*$. In polar solvents such as acetonitrile tertiary amines having a low oxidation potential are commonly considered to form triplet excited charge transfer complexes with $^3BP^*$ consisting of a contact pair of radical ions, CIP. The latter separate slightly and form solvent separated ion pairs (SSIP) that later can form free ions or undergo back-electron transfer or geminate proton transfer. The latter process results in the formation of a ketyl and an aminyl radical (see Scheme 1).

In non-polar solvents such as benzene the proton transfer occurs in the charge transfer complex because the radical ions cannot separate. Regarding primary and secondary amines, apart from charge transfer (CT) complex formation, also direct hydrogen abstraction as depicted in reaction (1) is possible, even in polar solvents.

$$^3BP^* + AH \rightarrow {}^{\bullet}BPH + A^{\bullet} \qquad (1)$$

According to Mataga et al. [20] in this case both processes, CT complex formation and direct hydrogen abstraction are competing at encounter of $^3BP^*$ and amine. The occurrence of charge transfer processes can be directly evidenced by detecting the free ions. This is attainable by recording the specific optical absorption spectrum of the radical ions or the increase in the electrical conductivity provided a solution containing BP and amine is exposed to light which is absorbed by BP. For example, free ions were detected in this way by UV irradiation of acetonitrile solutions containing BP and *N*,*N*-diethylaniline [5], BP and diphenylamine [14] or BP and 1,4-diazabicyclo[2,2,2]octane, DABCO [13,16,17].

The present paper deals with the reaction of hindered amines and corresponding amino ethers with triplet-excited benzophenone. Certain hindered amines, namely derivatives of 2,2,6,6-tetramethylpiperidine, are efficient light stabilizers for polyolefins [27–32] and it is commonly accepted that amino ethers are formed when hindered amine light stabiliz-

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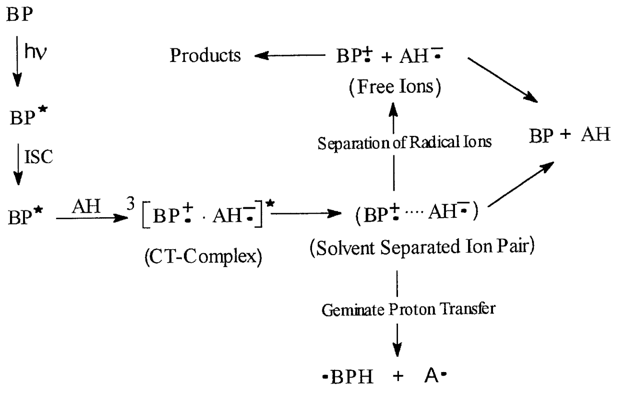
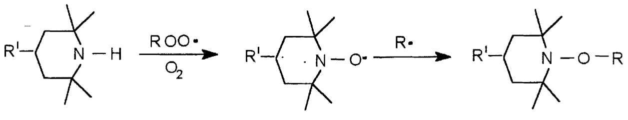


Scheme 1. Photoreaction of BP with amine in polar solvents.



Scheme 2. Conversion of hindered amine into amino ether.

ers (HALS), react with alkyl or peroxyl radicals as is shown in Scheme 2.

The high stabilizer efficiency of HALS compounds is thought to be particularly due to the capability of amino ethers to react with peroxyl radicals thus regenerating nitroxides that in turn can react with radicals. Due to the important role hindered amines play in polymer stabilization the interest in this class of compounds is growing. Following this line the present study concentrating on the reactivity of hindered amines and amino ethers was initiated. The chemical structures of the compounds examined in this work are presented in Tables 1 and 2.

Some of the compounds were studied by Step et al. [22] who inferred from transient absorption and time-resolved ESR measurements that ^{3}BP* is quenched quite effectively by amines **I** and **II** but does not react with the amino ether **III** [22]. Therefore, it was concluded that there is no significant interaction via charge transfer complex formation between amino ethers and ^{3}BP*.

Notably, Kluge and Brede have studied the photoreduction of BP by the hindered amines **IV** and **V** in various solvents including acetonitrile by flash photolysis using time-resolved optical absorption spectroscopy [26]. In that work no evidence for the benzophenone radical anion indicating the generation of free ions was found. By contrast, the generation of free ions with hindered amines was evidenced in the present work by performing time-resolved electrical conductivity measurements.

2. Experimental details

2.1. Materials

The compounds **I**, **II**, **III**, **XII**, **XIII** and **XIV** were obtained from Ciba-Geigy, Ardsley, NY. Compounds **IV**–**IX** were purchased from Aldrich. BP was obtained from E. Merck and was recrystallized from ethanol solution. Acetonitrile (Baker) was distilled prior to use.

2.2. Flash photolysis

A ruby laser (Korad, model K 1QS2) operated in conjunction with a frequency doubler was used to generate 20 ns flashes of 347 nm light. As in the previous work [17], for emission measurements, a RCA 1028 photomultiplier was used in conjunction with a gating system that operated the full chain of dynodes after a chosen delay period (100–800 ns) [33]. Photocurrent measurements were performed with a rectangular quartz cell attached to a flow system. The cell was equipped with a pair of platinum electrodes that were connected to a dc set-up [5]. The solutions were purged with argon prior to irradiation. Actinometry was performed with solutions of BP containing naphthalene as described previously [34].

2.3. Free ion quantum yields

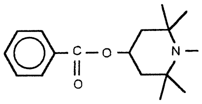
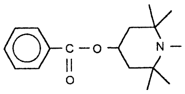
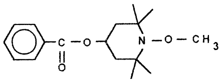
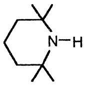
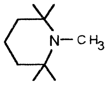
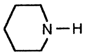
Quantum yield determinations on the basis of photocurrent measurements generally suffer from lack of knowledge concerning the mobility of the various ions or ion radicals. To circumvent this difficulty all photocurrent data were related to the photocurrent measured under identical conditions for the system BP/DABCO/acetonitrile and, consequently, $\Phi(\text{ion})_{\text{rel}}$ values are reported in this paper. The photoreduction of ^{3}BP* by DABCO does not yield ketyl radicals but essentially results in the formation of free radical ions. Very large free ion yields of the photoreduction of ^{3}BP* by DABCO have been reported in the literature: $\Phi(\text{ion}) = 0.8$ [16], $\Phi(\text{ion}) = 0.95$ [13] and $\Phi(\text{ion}) = 0.9$–1.0 [17].

3. Results

3.1. Free ion generation in the absence of amines and amino ethers

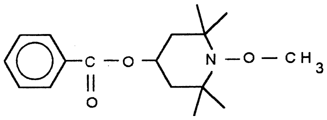
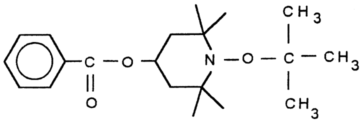
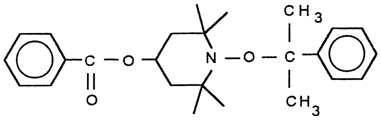
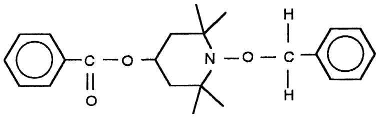
Upon irradiation of an Ar-saturated acetonitrile solution containing BP (2.3×10^{-3} mol dm^{-3}) and no other solute a photocurrent was built up within a few microseconds after the flash, indicating that the free ions are generated by a monophotonic process. Provided the free ions were generated by a biphotonic effect the photocurrent should be formed within the flash. Although rather low, the ion yield clearly surpassed the detection limit. $\Phi(\text{ion})_{\text{rel}} = 0.015$ was obtained at an absorbed dose per flash $D_{\text{abs}} = 9 \times 10^{-5}$ einstein dm^{-3}. In this connection it is notable that the photogeneration of free ions from BP in acetonitrile has been reported recently by Raumer et al. [35] who performed irradiations at $\lambda_{\text{exc}} = 355$ nm and concluded on the basis of the results of detailed experimental work

Table 1
Photoreduction of benzophenone by amines. Solvent: acetonitrile. $[BP] = 2.3 \times 10^{-3}$ mol dm^{-3}; $D_{abs} = 3.6 \times 10^{-5}$ einstein dm^{-3}

Amine	E_{ox}[a] (V)	IP[b] (eV)	k_q[c] (dm^3 mol^{-1} s^{-1})	Φ(ion)$_{rel}$[d]
 **I**	1.18[e]		7.6×10^8	0.018
 **II**	0.84[e]		4.7×10^9	0.074
 **III**	1.25[e]		1.7×10^6	0.10
 **IV**		8.04[f]	1.4×10^9 2.5×10^9[k]	0.035
 **V**		7.68[f]	6.4×10^9 6.2×10^9[k]	0.096
 **VI**		8.70[f] 8.66[g]	3.0×10^9	0.052
$(C_2H_5)_2N\text{–}H$ **VII**	1.3[h]	8.63[g]		0.125
$N(C_2H_5)_3$ **VIII**	0.98[h]	8.08[g]	3.0×10^9	0.54
DABCO **IX**	0.56[h]	7.70[i]	1.2×10^{10}	1.0
None			–	0.015[j]

[a] Oxidation potential versus SCE.
[b] Vertical ionization potential.
[c] Rate constant of phosphorescence quenching.
[d] Quantum yield of free ions relative to that of the system BP/DABCO.
[e] Oxidation peak potential of cyclic voltammogram.
[f] Ref. [39].
[g] Ref [38].
[h] Ref. [37].
[i] Ref. [12].
[j] $D_{abs} = 9.0 \times 10^{-5}$ einstein dm^{-3}.
[k] Ref. [26].

Table 2
Quenching of BP phosphorescence by hindered amino ethers. Solvent: acetonitrile $[BP] = 2.3 \times 10^{-3}$ mol dm^{-3}; $D_{abs} = 3.6 \times 10^{-5}$ einstein dm^{-3}

Amine	k_q (dm^3 mol^{-1} s^{-1})	E_p^a (V)[a]
 **III**	1.7×10^6	1.25
 **XII**	ca. 1×10^6	1.41
 **XIII**	6.0×10^7	1.38
 **XIV**	4.3×10^7	1.73

[a] Oxidation peak potential from cyclic voltammograms recorded with Pt electrodes in 0.1 M $Bu_4N^+PF_6^-$ acetonitrile solution versus the saturated calomel electrode (SCE), calibrated versus the ferrocene/ferrocenium couple ($E_p^a = 0.31$ V). Courtesy of Prof. W. Abraham.

that ion generation in this system is due to triplet–triplet annihilation (TTA):

$$^3BP^* + {}^3BP^* \rightarrow BP^{\bullet +} + BP^{\bullet -} \qquad (2)$$

This implies that $\Phi(\mathrm{ion})_{\mathrm{rel}}$ is not independent of D_{abs}, the absorbed dose per flash, but increases with increasing D_{abs}. Taking this into account a $\Phi(\mathrm{ion})_{\mathrm{rel}}$ value quite similar to that found in this work is obtained on the basis of the data of Raumer et al. [35].

3.2. Reaction of BP triplets with amines

3.2.1. Phosphorescence quenching

The major feature of the exposure of BP, dissolved in acetonitrile, to 347 nm light is the rapid formation ($\tau \approx 20$ ps) of BP triplets with a rather high quantum yield ($\Phi(^3BP^*) \approx 1.0$) [36]. The decay of BP triplets can be readily monitored because of the characteristic optical absorption and emission (phosphorescence) spectra of $^3BP^*$. Notably, in the presence of most amines a substantial portion of the initially formed triplets is converted into ketyl radicals. Since the optical absorption spectra of ketyl radicals and BP triplets strongly overlap, the analysis of kinetic data based on absorption measurements is tedious. Such a problem does not exist as far as phosphorescence measurements are concerned, and, therefore, in the present work the kinetics of the reaction of $^3BP^*$ with amines were followed throughout by measuring the decay of the emission at 530 nm. Typical results are shown in Figs. 1 and 2. A phosphorescence decay trace, recorded in this case with compound **V**, is depicted in Fig. 1a and Fig. 2 shows plots of k_1, the pseudo-1st order rate constant of the phosphorescence decay, versus [quencher], the quencher concentration, obtained by using compounds **I**, **II** and **III** as quenchers. Quenching rate constants k_q were evaluated on the basis of Eq. (3):

$$k_1 = k_0 + k_q[\text{quencher}] \qquad (3)$$

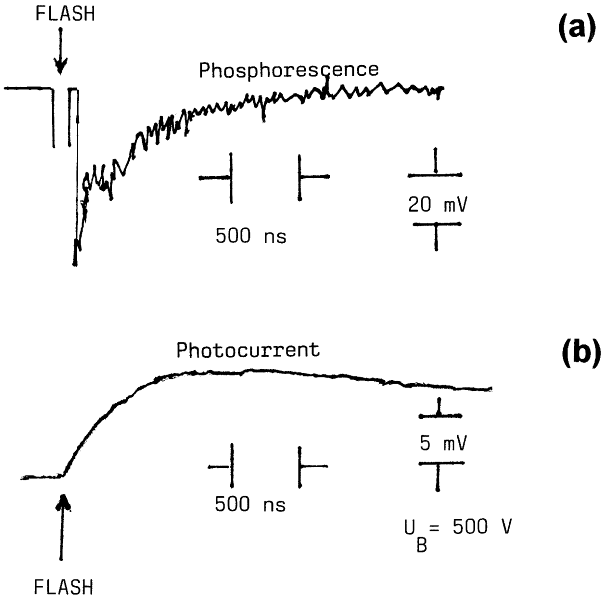


Fig. 1. Reduction of triplet-excited benzophenone by amine **V** in Ar-saturated acetonitrile solution at ambient temperature. Oscilloscope traces depicting the phosphorescence decay at $\lambda_{em} = 530$ nm (a) and the build-up of the photocurrent (b) after the 20 ns flash ($\lambda_{inc} = 347$ nm). [BP] = 2.3×10^{-3} mol dm^{-3}; [**V**] = 1×10^{-3} mol dm^{-3}; $D_{abs} = 3.6 \times 10^{-5}$ einstein dm^{-3}.

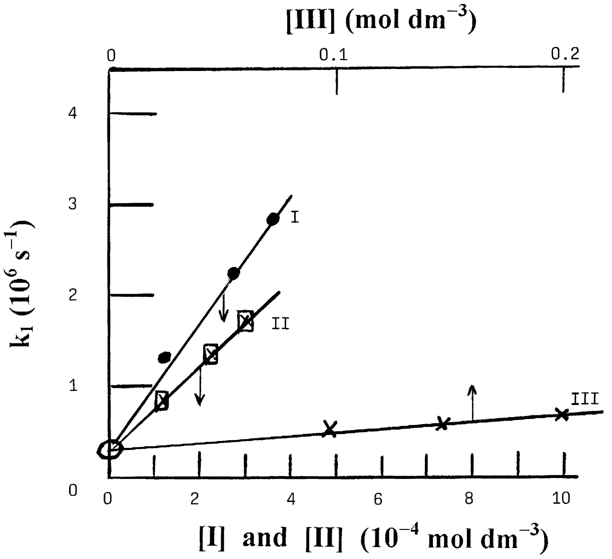


Fig. 2. Phosphorescence quenching of triplet-excited benzophenone by compounds **I**, **II** and **III** in Ar-saturated acetonitrile solution at ambient temperature. Plots of the 1st-order decay constant vs. the quencher concentration. $\lambda_{em} = 530$ nm; [BP] = 2.3×10^{-3} mol dm^{-3}; $D_{abs} = 3.6 \times 10^{-5}$ einstein dm^{-3}.

As can be seen from Table 1 all amines are less reactive towards $^3BP^*$ than DABCO, i.e. k_q is lower than in the case of DABCO ($k_q = 1.2 \times 10^{10}$ dm^3 mol^{-1} s^{-1}). Regarding the tertiary amines the k_q values of the piperidine type amines **II** and **V** are larger than that of triethyl amine (**VIII**). Notably, substitution of the 4-hydrogen by the benzoyl-oxy group in **IV** and **V** reduces the reactivity to some extent as is recognized by comparing the k_q values of compounds **IV** and **V** with those of compounds **I** and **II**, respectively. Moreover, it is inferred from the k_q values of the corresponding amine couples **I**/**II** and **IV**/**V**, that tertiary amines are more reactive towards $^3BP^*$ than secondary amines.

3.2.2. Photogeneration of free ions

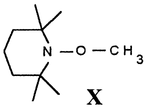
In acetonitrile solutions containing apart from BP also an amine, a photocurrent substantially larger than in the absence of amine, was formed after the flash concomitantly with the decay of the phosphorescence. This is demonstrated by a typical oscilloscope trace recorded in this case with amine **V** shown in Fig. 1b. Here, only about 10% of the triplets initially formed are estimated to undergo TTA (with $k_{TTA} = 1.8 \times 10^{10}$ dm^3 mol^{-1} s^{-1}, $k_q = 6.4 \times 10^9$ dm^3 mol^{-1} s^{-1}, [$^3BP^*$] = 3.6×10^{-5} mol dm^{-3} and [**V**] = 1×10^{-3} mol dm^{-3}). Therefore, contributions to the photocurrent arising from TTA (vide Section 3.1) are negligible.

The photoreduction of BP triplets by amines results in the formation of free ions in all cases. However, the yields differ significantly as can be seen from Table 1. Generally, secondary give lower ion yields than tertiary amines. The piperidine type amines **IV** and **V** yield four to six times less free ions than the corresponding ethyl amines **VII** and **VIII**, respectively. Substitution of the 4-hydrogen by the benzoyl-oxy group in **IV** and **V** results in a 2- and 1.3-fold decrease in the ion yield (compare **IV** with **I**, and **V** with **II**). Moreover, substitution of the 2- and 6-hydrogens by methyl groups reduces the ion yield by a factor 1.5 (compare **IV** with **VI**).

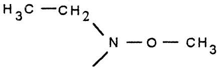
3.3. Reaction of BP triplets with amino ethers

3.3.1. Phosphorescence quenching

Experiments with compounds **X** and **XI**, that were synthesized for this work, did not yield reproducible



X



XI

results. It turned out that these amino ethers are not very stable and spontaneously form products capable of reducing BP triplets. On the other hand, compounds **XII–XIV** (see Table 2) are quite stable. At low concentration they affect the benzophenone phosphorescene decay only scarcely and, therefore, relatively high amine concentrations (>5 × 10^{-2} mol dm^{-3}) had to be applied to measure quenching rate constants. The latter range from 10^6 to 10^7 dm^3 mol^{-1} s^{-1}, as can be seen from Table 2. The values of these rate constants are much lower than those pertaining to the corresponding amines (see Table 1). Therefore, it can be now concluded more precisely than before [22], that amino ethers do react with ^{3}BP*, but their reactivity towards ^{3}BP* is much lower than that of the corresponding amines. Interestingly, the benzyl ethers **XIII** and **XIV** are much more reactive towards ^{3}BP* than the methyl or the *tert*-butyl ether, compounds **III** and **XII**, respectively, as indicated by a difference in k_q values of one order of magnitude.

3.3.2. Photogeneration of free ions

Electrical conductivity measurements revealed the photogeneration of free ions in acetonitrile solutions containing BP and amino ethers. However, with all compounds listed in Table 2 the photocurrent formed several times more rapidly than the phosphorescence decayed. Typical kinetic traces (recorded in this case with the system **III**/BP) demonstrating this behavior are shown in Fig. 3. The pronounced difference in the rates of the photocurrent generation and phosphorescence decay indicates that the formation of free ions is not correlated with a reaction of the amino ether with ^{3}BP*. It rather seems that the photocurrent reflects the generation of radical ions by TTA and/or ionic species formed in consecutive reactions of the radical ions with the amino ether. This conjecture is substantiated by the fact that the generation rate of the current increased with increasing amino ether concentration. Actually, at the absorbed dose $D_{abs} = 9.0 \times 10^{-5}$ einstein dm^{-3} applied in this case about 25% of the BP triplets initially formed are estimated to undergo TTA.

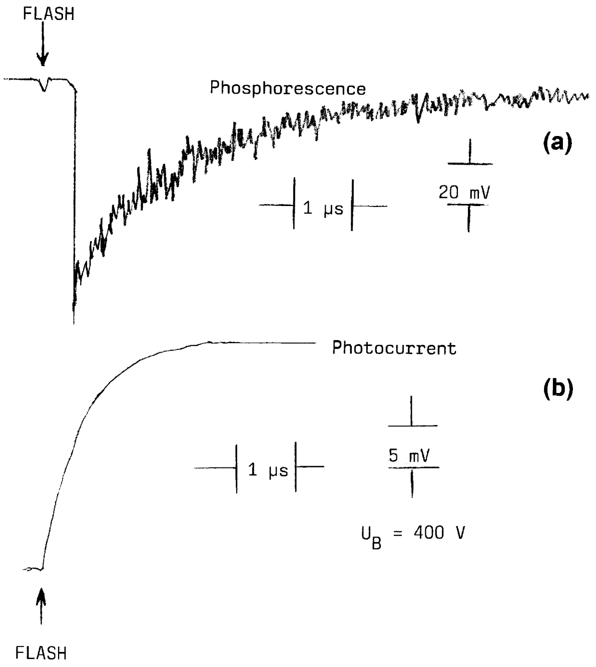


Fig. 3. Reaction of triplet-excited benzophenone with amino ether **III** in Ar-saturated acetonitrile solution at ambient temperature. Oscilloscope traces depicting the phosphorescence decay at $\lambda_{em} = 530$ nm (a) and the build-up of the photocurrent (b) after the 20 ns flash ($\lambda_{inc} = 347$ nm). [BP] = 2.3 × 10^{-3} mol dm^{-3}; [**III**] = 5.0 × 10^{-2} mol dm^{-3}; $D_{abs} = 9.0 \times 10^{-5}$ einstein dm^{-3}.

4. Discussion

4.1. Reaction of ^{3}BP* with amines

The most important result of this work concerns the fact that free ions are formed upon irradiation of acetonitrile solutions containing BP and one of the amines listed in Table 1. Therefore, it can be concluded that these amines interact with BP triplets via a charge transfer mechanism. In the following, the dependence of k_q, the quenching rate constant, and of $\Phi(\text{ion})_{rel}$, the quantum yield of free ion formation, on the chemical nature of the amines will be discussed in some detail.

4.1.1. Dependence of k_q and $\Phi(\text{ion})_{rel}$ on the chemical nature of the amine

The rate constants of the reaction of ^{3}BP* with amines have been reported to increase with decreasing ionization potential (IP) (or oxidation potential, E_{ox}) of the amine and to approach eventually a limiting value corresponding to about $1\times10^{10}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$ [18]. This behavior is in accordance with the model of Rehm and Weller [40] and on this basis it can be explained why secondary amines are less reactive than the corresponding tertiary amines. Actually, values of IPs or oxidation peak potentials (E_p^a) are available in the cases of the couples **IV**/**V** and **I**/**II**, respectively (vide Table 1). In both cases, the values of IP or E_p^a of the more reactive tertiary amines **V** and **II** are lower than those of the less reactive secondary amines **IV** and **I**.

Apparently, a similar trend exists regarding the probability of the formation of free ions from CT complexes. As has been pointed out above (vide Section 3.3.2 and Table 1) the $\Phi(\mathrm{ion})_{rel}$ values pertaining to secondary amines are lower than those of the corresponding tertiary amines.

In this connection it is interesting to note, that according to Miyasaka and Mataga [20] the rate constant of geminate proton transfer decreases with decreasing oxidation potential in the case of tertiary amines. With the aid of the data compiled in Table 1 this conclusion is substantiated in the cases of **VIII** and **IX** by the corresponding values, i.e. $\Phi(\mathrm{ion})_{rel}$ (0.54 versus 1.0) and E_{ox} (0.98 versus 0.56). Here, it is presumed that an increase in $\Phi(\mathrm{ion})_{rel}$ is correlated to a decrease in the yield of ketyl/aminyl radical formation. However, this correlation does not seem to be of general importance, as can be seen by comparing the $\Phi(\mathrm{ion})_{rel}$ values of **V** and **VIII**. In the case of **V** $\Phi(\mathrm{ion})_{rel}$ is about five times lower than for **VIII**, although IP(**V**) is lower than IP(**VIII**).

Apart from these thermodynamic considerations a mechanistic aspect should also be taken into account here, namely the fact that in the case of the tertiary amines two competing processes have to be envisaged with respect to the formation of free ions according to Scheme 1: proton transfer and ion recombination (back electron transfer). In the case of the secondary amines, on the other hand, also direct H-abstraction according to reaction (1) has to be taken into account. This reaction is likely to participate in the process on the expense of free ion generation and, therefore in the case of secondary amines $\Phi(\mathrm{ion})_{rel}$ should be lower than for tertiary amines.

4.2. .Reaction of ^{3}BP* with amino ethers

Apparently, the amino ethers examined in this work interact relatively weakly with BP triplets. This is concluded from the fact that phosphorescence quenching occurs relatively slowly, i.e. with rate constants ranging from 1×10^6 to $6\times10^7\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$. The relatively low reactivity is in accordance with rather high oxidation peak potentials (vide Table 2). However, the rather large difference in the k_q values of the alkyl ethers **III** and **XII** and the benzyl ethers **XIII** and **XIV** is not reflected by a corresponding difference in E_p^a values and a plausible explanation for this difference cannot be given at present.

Notably, the formation of a photocurrent accompanying the phosphorescence decay could not be seen, although a relatively large photocurrent was observed with all amino ethers. But it built up much faster than the phosphorescence decayed. Thus, the free ions formed in this case must originate from a different source. This might be based on triplet–triplet annihilation which presumably is not or only scarcely affected by amino ethers. Here, it is recalled that the generation of free ions via TTA by laser flash photolysis of BP in acetonitrile via reaction (2) has been evidenced [35]. When a solution containing BP and amino ether **III** ($0.1\,\mathrm{mol\,dm^{-3}}$) was exposed to a laser flash ($D_{abs}=3.6\times10^{-5}\,\mathrm{einstein\,dm^{-3}}$) a photocurrent about 10 times larger than in the absence of **III** was measured. A plausible explanation is based on the following mechanism which assumes that **III** reacts with $\mathrm{BP}^{\bullet+}$ and in this way impedes to some extent the neutralization reaction (5):

$$^3\mathrm{BP}^* + {}^3\mathrm{BP}^* \rightarrow \mathrm{BP}^{\bullet+} + \mathrm{BP}^{\bullet-} \quad (2)$$

$$\mathrm{BP}^{\bullet+} + \mathbf{III} \rightarrow \mathrm{BP} + \mathbf{III}^{\bullet+} \quad (4)$$

$$\mathrm{BP}^{\bullet+} + \mathrm{BP}^{\bullet-} \rightarrow \mathrm{BP} + \mathrm{BP} \quad (5)$$

Provided only **III** and $\mathrm{BP}^{\bullet-}$ are competing for $\mathrm{BP}^{\bullet+}$ the probability p_{ET4} for the occurrence of the electron transfer reactions (4) is given by Eq. (6):

$$p_{ET4} = \frac{k_{ET}[\mathbf{III}]}{k_{ET}[\mathbf{III}] + k_n[\mathrm{BP}^{\bullet+}]} \quad (6)$$

With $k_{ET}=5\times10^9\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$, $k_n=2\times10^{10}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$, $[\mathbf{III}]=0.1\,\mathrm{mol\,dm^{-3}}$ and $[\mathrm{BP}^{\bullet+}]=10^{-5}\,\mathrm{mol\,dm^{-3}}$ one obtains: $p_{ET4}\approx1.0$, i.e. ET (reaction (4)) is highly favored over neutralization (reaction (5)). Apart from the prevention of the neutralization reaction the increase in the photocurrent i_{total} might be also due to the decomposition of $\mathbf{III}^{\bullet+}$ into more mobile fragments, because i_{total} is proportional to the mobility μ_i of the charge carriers i according to Eq. (7):

$$i_{total} \propto \left(\frac{E}{d}\right)\sum(q_i c_i \mu_i) \quad (7)$$

where, q_i is the charge of the ions, c_i the concentration of ions, E the applied electric field strength and d the distance between electrodes.

5. Conclusions

The experiments described in this paper show that hindered amines such as 2,2,6,6-tetramethyl piperidines and *N*-methyl-2,2,6,6-tetramethyl piperidines are much more reactive towards triplet excited benzophenone (^{3}BP*) than hindered amino ethers such as *N*-methoxy-2,2,6,6-tetramethyl piperidines. The rate constants determined by phosphorescence quenching differ by two to three orders of magnitude. From electrical conductivity measurements it is inferred that a charge transfer mechanism becomes operative in the reaction of ^{3}BP* with the amines only but not in the reaction of ^{3}BP* with the amino ethers.

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