

## 55. Photoreduction of Triplet Benzophenone by Tertiary Amines: Amine Molecular Structure and Ketyl Radical Yield

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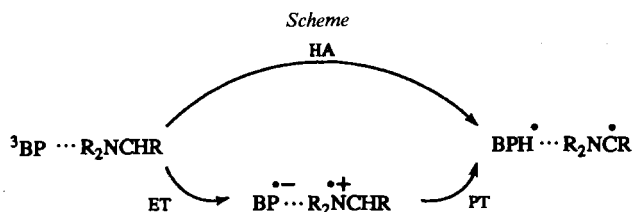
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Dedicated to Professor *Fabian Gerson* on the occasion of his retirement, in grateful appreciation of his contributions to science and to education

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The photoreduction of triplet benzophenone by 14 tertiary amines was investigated. The ketyl radical yields do not correlate with the quenching rate constants, nor with the electron donor propensity of the amines. Individual structural features of the amines seem to determine the photoreduction yields.

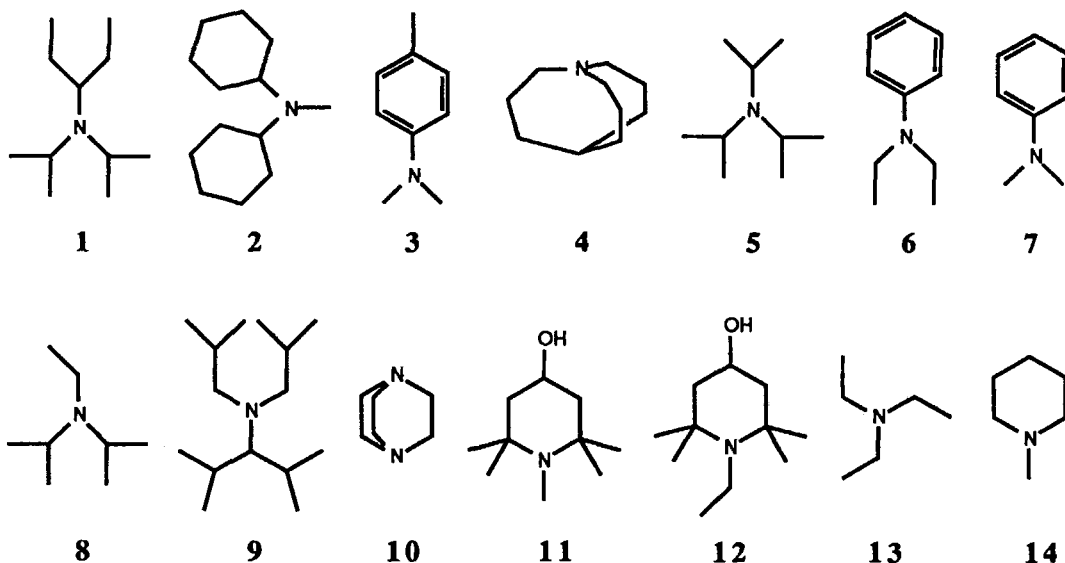
**Introduction.** – The photoreduction of triplet benzophenone ( $^3\text{BP}$ ) by tertiary amines is a well-known reaction which has been extensively investigated [1–3]. Basically, two different reaction mechanisms were proposed as shown in the *Scheme*: direct hydrogen abstraction (HA) or electron transfer (ET) followed by proton transfer (PT). Both mechanisms lead to the same products: the ketyl radical ( $\text{BPH}$ ) of  $\text{BP}$ , and a C( $\alpha$ )-centered radical being stabilised by two-center three-electron bonding involving the N-atom lone-pair. While HA dominates quenching by secondary amines [4], the ET-PT mechanism is generally assumed to prevail for tertiary amines with available H-atoms at C( $\alpha$ ) [1] [5–7] in a polar environment.



For the latter case, the correlation between ET driving force ( $\Delta G_{\text{ET}}$ ) and  $\text{BPH}$  yield ( $\phi_{\text{BPH}}$ ) was investigated in [4] [8] where the PT rate constants ( $k_{\text{PT}}$ ) were found to decrease with increasing driving force. This behaviour was explained by assuming that the ET distance increases in this direction. However, with increasing interionic distance in the intermediate ET complex the subsequent nearly diffusion-controlled PT loses its efficiency. Hence, alternative reaction channels other than PT become competitive.

Recently, we reported about some tertiary amines which do not photoreduce  $^3\text{BP}$  [9], which we traced to their special molecular structure. The present work compares a great number of tertiary amines as shown below with respect to their propensity of photore-

duction. Specifically, the yields of ketyl radical ( $\phi_{\text{BPH}}$ ) are correlated with the ionisation potentials ( $IP$ ) of the amines and the observed quenching rate constants ( $k_q$ ) in polar solvents.



**Experimental.**—A classical flash photolysis setup was used for the determination of  $k_q$  and  $\phi_{\text{BPH}}$ . The excitation sources were a frequency-tripled Q-switched ns-Nd:YAG laser (*JK Lasers 2000*) generating 19-ns pulses at 355 nm of 6-mJ energy for the determination of  $\phi_{\text{BPH}}$ , and a subnanosecond nitrogen laser (*LN100*) generating pulses at 337 nm of 100  $\mu\text{J}$  energy for the determination of  $k_q$ . Both lasers were operated at 10-Hz repetition rate. All measurements were made in MeCN. The **BP** solns. (5 mM) had an absorbance of 0.5 at 355 nm, and of 0.78 at 337 nm, and were deoxygenated by bubbling Ar for 15 min.

The values for  $k_q$  were extracted from the  $^3\text{BP}$  phosphorescence lifetimes by applying the *Stern-Volmer* treatment. Those for  $\phi_{\text{BPH}}$  were obtained by comparing the transient absorption signals at 540 nm with the **BP**/benzhydrol reference system ( $\phi_{\text{BPH}} = 2$  [6] [10], and  $k_q = 4.5 \cdot 10^6 \text{ M}^{-1}\text{s}^{-1}$ ). For **BP/13**, two earlier values for  $\phi_{\text{BPH}}$  are reported ( $\phi_{\text{BPH}} = 0.73$  [4] and  $\phi_{\text{BPH}} = 1$  [6] [10]). Our work yields a value of 0.91, which we used as reference for all other measurements. The quencher concentrations were adjusted so that at least 99% of  $^3\text{BP}$  were deactivated by the photoreduction pathway.

The  $IP$ 's were recorded with a modified *Perkin-Elmer PS 16* photoelectron spectrometer and the adiabatic ionisation potentials  $IP_a$  determined by the tangential extrapolation technique (see the *Table*).

The amines **4** and **5** were synthesised according to the literature [11] [12], and **11** and **12** were provided by *Ciba-Geigy SA*, Marly. The other amines are commercially available and were appropriately purified before use. **BP** (*Aldrich*, Gold Label) and **DABCO** (**10**) were sublimed before use. MeCN (*Fluka*, UV-grade) was used as such.

**Results and Discussion.**—The reaction free energy  $\Delta G_{\text{ET}}$  of a bimolecular ET reaction can be estimated with the *Rehm-Weller* equation

$$\Delta G_{\text{ET}} = E_{\text{ox}}(\mathbf{D}) - E_{\text{red}}(\mathbf{A}) - E^* + C$$

with  $E_{\text{ox}}(\mathbf{D})$  being the oxidation potential of the donor amines (**D**),  $E_{\text{red}}(\mathbf{A})$  the reduction potential of the acceptor **A** = **BP**, and  $E^*$  the triplet energy of **BP**.  $C$  is the *Coulomb* term which takes into account the electrostatic interaction in the incipient ion pair after ET.

Table. Geminate Ion Pair yields  $\phi_{\text{gip}}$ , Quenching Constants  $\log(k_q)$  and Photoreduction Yields  $\phi_{\text{BPH}}$  for the Quenching of  $^3\text{BP}$  by Tertiary Amines in MeCN. The donor propensity of the amines is indicated by their adiabatic and vertical ionisation potentials ( $IP_a$  and  $IP_v$ , resp.).

Amine	No.	$IP_a^{\text{a)}}$ [eV]	$IP_v^{\text{b)}}$ [eV]	[Amine]/ for $k_q^{\text{c)}}$	$\cdot 10^{-4}\text{M}$ for $\phi_{\text{BPH}}$	$\phi_{\text{gip}}^{\text{d)}}$	$\log(k_q)$	$\phi_{\text{BPH}}^{\text{e)}}$
<i>N,N</i> -Diisopropylpentan-3-amine	1	6.85	7.2	1.8	92	99.3	9.86	0.0 <sup>f)</sup>
<i>N</i> -Ethylidicyclohexylamine	2	6.85	7.35	2.4	159	99.1	9.65	0.93
<i>N,N</i> -Dimethyl- <i>p</i> -toluidine	3	6.9 <sup>g)</sup>	7.26 <sup>g)</sup>	1.7	83	99.1	9.94	0.71
1-Azabicyclo[3.3.3]undecan (Manxine)	4	6.95 <sup>h)</sup>	7.13 <sup>h)</sup>	1.8	87	99.4	9.94	1.01
Triisopropylamine	5	6.95	7.2	1.6	87	99.3	9.89	0.0 <sup>f)</sup>
<i>N,N</i> -Diethylaniline	6	6.95 <sup>i)</sup>	7.2 <sup>i)</sup>	2.3	104	99.1	9.84	0.58
<i>N,N</i> -Dimethylaniline	7	7.1 <sup>j)</sup>	7.45 <sup>i)</sup>	2.1	84	99.1	9.93	0.99
<i>N</i> -Ethyl-diisopropylamine	8	7.2	7.7	3.2	160	99.1	9.67	1.02
<i>N,N</i> -Diisobutyl-2,4-dimethylpentan-3-amine	9	7.2	7.7	3.6	589	99.0	9.06	1.14
1,4-Diazabicyclo[2.2.2]octan (DABCO)	10	7.24 <sup>h)</sup>	7.52 <sup>h)</sup>	1.5	149	99.6	9.89	0.0 <sup>f)</sup>
4-Hydroxy-1,2,2,6,6-pentamethyl-piperidine	11	7.25	7.75	4.0	272	99.3	9.40	0.99
<i>N</i> -Ethyl-4-hydroxy-2,2,6,6-tetramethyl-piperidine	12	7.25	7.67	4.6	219	99.3	9.50	0.65
Triethylamine	13	7.5	8.05	4.3	397	99.1	9.23	0.91
<i>N</i> -Methylpiperidine	14	7.8 <sup>k)</sup>	–	8.1	368	99.1	9.26	1.07

a)  $IP_a$  corresponds to the onset of the photoelectron band as determined by the tangential extrapolation method [15].

b) If no literature reference is quoted, the  $IP$ 's were measured in our institute.

c) This value corresponds to the highest concentration employed for the Stern-Volmer plots.

d) The geminate ion pair yield ( $\phi_{\text{gip}}$ ) corresponds to the percentage of triplet quenched by the amine.

e) See *Experimental*.

f) [9].

g) [16].

h) [17].

i) [18].

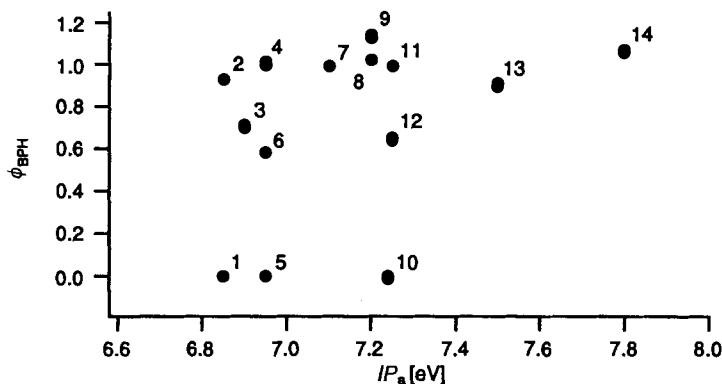
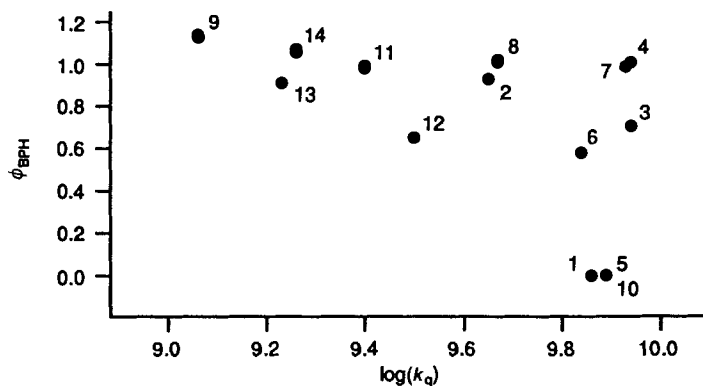
k) [19].

Only few reversible oxidation potentials of amines are available. The gas phase  $IP$ 's are readily and accurately accessible by PE spectroscopy. As reflected by their low  $IP$ 's (see *Table*), amines are easily oxidised and are, therefore, good electron donors. This is also expressed by the almost diffusion limited  $k_q$ 's as shown in the *Table*.

Previous work [5] [7] [13] [14] with ps-time resolution was complicated by the use of high amine concentrations. The excitation of ground state complexes as well as the interception of excited  $^1\text{BP}$  by the amines may generate different types of ion pairs with their own reaction dynamics. This problem is eliminated in the present work by using low amine concentrations (see *Table*), which is possible because of the  $\mu\text{s}$ -lifetime of  $^3\text{BP}$  and the observation of the reactions in the  $\mu\text{s}$ -time scale.

The values for  $\phi_{\text{BPH}}$  are plotted vs. *i*)  $IP_a$ , and *ii*)  $\log(k_q)$  in *Figs. 1* and *2*, respectively. No correlation is discernable in either case.

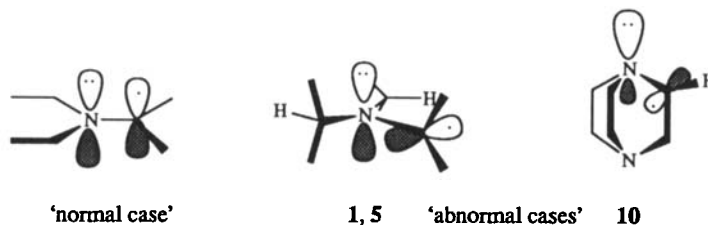
*i*) For the two amines with the lowest  $IP_a$ , **1** and **2**, two completely different results for  $\phi_{\text{BPH}}$  were found: essentially nil for **1**, and almost unity for **2**. With the exception of

Fig. 1. Plot of  $\phi_{BPH}$  vs. the  $IP_a$ 's of the aminesFig. 2. Plot of  $\phi_{BPH}$  vs.  $\log(k_q)$ 

**1, 5 and 10**, all other tertiary amines did photoreduce  $^3BP$  with an efficiency independent of their  $IP_a$ . This stands in contrast to the conclusions in [4] [8], which admittedly were based on a very limited set of data.

ii) The observed values for  $\phi_{BPH}$  do also not correlate with the quenching rate constants  $\log(k_q)$ . Thus, for the examples with the highest five  $k_q$ 's, either very efficient (**4, 7**), or intermediate (**3**), or no photoreduction (**5, 10**) is observed.

As in *i* above, the three amines **1, 5** and **10** call for special attention. It appears as if they do not photoreduce  $^3BP$  due to their special molecular structure. As already mentioned in [9], no stabilizing two-center three-electron bond (*i.e.*, 'normal case') can be formed in these 'abnormal cases' as shown below:



Manxine (**4**), an amine with three essentially coplanar N–C bonds [11], should by analogy with the above mentioned compounds not engage in PT after ET. However, to our surprise it photoreduces <sup>3</sup>BP efficiently. Molecular models suggest that **4** is a relatively flexible molecule with respect to a distortion about the three-fold symmetry axes, leading from idealized  $C_{3v}$  to  $C_3$  symmetry. Hence, after H-abstraction at C( $\alpha$ ) at least a partial stabilising two-center three-electron bond can evolve which is not possible in **10** due to its  $D_{3h}$  symmetry. Of interest is also the comparison between **11** and **12**: the Me group in **11** can rotate freely, whereas the Et group in **12** is conformationally fixed in an ‘out of plane’ situation due to steric interference with the four Me groups at the C(2)- and C(6)-positions of the piperidine ring. By analogy with **1**, **5** and **10**, this results in an unfavourable outcome for a two-center three-electron bond after ET and subsequent PT, which finds its expression in a lower  $\phi_{\text{BPH}}$  as compared to **11**.

**Conclusions.** – ET Phenomena can be studied with two focuses in mind with regard to the properties of the chemical systems employed: *a*) understanding the ET quenching process, or *b*) understanding the ensuing chemical transformations. For bimolecular ET reactions the well-known *Rehm-Weller* curve results if quenching rate constants  $k_q$  are plotted vs. driving forces  $\Delta G_{\text{ET}}$ . However, in studies employing a common excited acceptor **A** it has been found that ‘multiple’ *Rehm-Weller* curves result if different classes of quenchers **D** are compared, such as olefinic with aromatic hydrocarbon  $\pi$ -systems, or aliphatic with aromatic amines [20]. It was argued that, given equal values for  $E_{\text{ox}}(\mathbf{D})$ , different *Coulomb* energies for the ion pair resulting after ET are responsible for this outcome. This is related to the electronic structure of the **D**’s before ET, which determines the positive hole distribution in the donor cations **D**<sup>+</sup> after ET.

The present work concentrates on tertiary amines which are, chemically speaking, ‘one class of donors **D**’. Their oxidation propensity upon ET quenching of <sup>3</sup>BP does not allow insight into *a* as all observed rate constants lie in the diffusion controlled regime. Future work with weaker acceptors than <sup>3</sup>BP will shed light on this question. With regard to *b*) on the other hand, the photoreduction efficiency of the amines does not correlate with the parameters which govern ET quenching efficiency. We conclude that particular features of their molecular structure are responsible which find their expression only in the transition state for PA which follows ET.

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