

## Quenching of $n,\pi^*$ -Excited States in the Gas Phase: Variations in Absolute Reactivity and Selectivity

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Received March 18, 2002. Revised Manuscript Received June 26, 2002

**Abstract:** The quenching of the  $n,\pi^*$ -excited azoalkane 2,3-diazabicyclo[2.2.2]oct-2-ene by 19 heteroatom-containing electron and hydrogen donors, that is, amines, sulfides, ethers, and alcohols, was investigated in the gas phase. Deuterium isotope effects were measured for 9 selectively deuterated derivatives. The data support the involvement of an excited charge-transfer complex, that is, an exciplex, for tertiary amines and sulfides, and a competitive direct hydrogen transfer from the C–H bonds of ethers or from the N–H or O–H bonds of secondary and primary amines or alcohols. The recently observed “inverted” solvent effect for the fluorescence quenching of azoalkanes by amines and sulfides in solution is supported by the observed rate constants in the gas phase, which are substantially larger than those in solution. A more pronounced inverted solvent effect for the weaker electron-donating sulfides and a presumably faster exciplex deactivation result in a switch-over in absolute reactivity relative to tertiary amines in the gas phase. Most importantly, the kinetic data demonstrate that the reactivity of the strongly dipolar O–H and N–H bonds in photoinduced hydrogen abstraction reactions shows a larger decrease upon solvation than that of the less polar C–H bonds. The azoalkane data are compared with previous studies on quenching of  $n,\pi^*$ -triplet-excited ketones in the gas phase.

### Introduction

The photoreactions of  $n,\pi^*$ -excited ketones and azoalkanes with amines, sulfides, ethers, and alcohols can be understood as a competition between charge transfer (CT) to form exciplexes or radical ion pairs and hydrogen transfer to form radical pairs.<sup>1–7</sup> Solvent effects have been investigated to elucidate the relative contributions of the various reaction pathways and, in particular, to test for the formation of radical ion pairs, which should be strongly disfavored in nonpolar solvents. We have recently communicated an “inverted” solvent effect for the fluorescence quenching of  $^1n,\pi^*$ -excited 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO) by amines.<sup>7–9</sup> Although this photoreaction involves the formation of exciplexes with partial CT,<sup>6–10</sup> it is accelerated in nonpolar solvents because the highly dipolar excited chromophore experiences a relative stabilization in polar solvents, thereby retarding the quenching process.<sup>8</sup>

The importance of solvent effects for the mechanistic understanding of the quenching of  $n,\pi^*$ -excited states encourages the study of these basic photoreactions in the absence of solvation, that is, in the gas phase. However, the study of quenching of  $n,\pi^*$ -excited states in the gas phase has been restricted to case studies.<sup>11–18</sup> Moreover, the vapor pressure of benzophenone, which is the most extensively studied ketone in solution, is too low to allow gas-phase studies at room temperature. We have presently employed DBO to gain further insight into gas-phase photoreactivity. The strongly fluorescent DBO is photophysically well characterized<sup>19</sup> and sufficiently volatile even at room temperature to permit gas-phase quenching studies, the first of which were reported by Steel.<sup>20</sup> This provides the exceptional opportunity to study quenching in both the gas phase and in solution under identical conditions with standard laser-flash photolysis equipment. Moreover, the fluorescence lifetime of DBO in the gas phase amounts to 1  $\mu$ s, which opens

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a wide dynamic range to quantify the photoreactivity even with weak hydrogen or electron donors. The data are compared to those obtained for  $n,\pi^*$ -excited ketones.

## Experimental Section

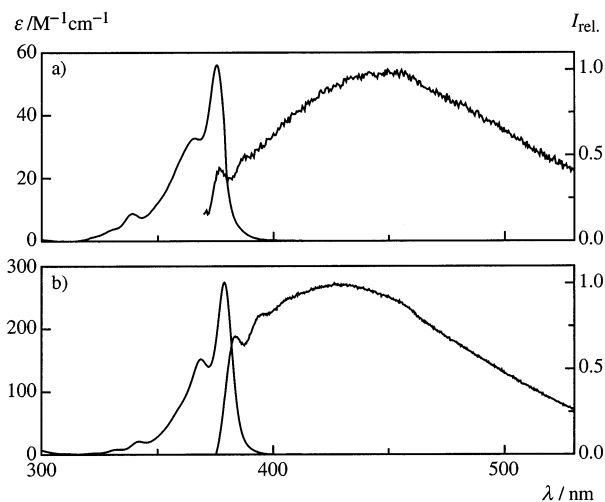
**Materials.** DBO was synthesized according to a literature procedure and purified by sublimation and subsequent recrystallization from *n*-hexane.<sup>21</sup> All amines were from Fluka or Aldrich (>99%), and liquid ones were further purified by distillation. The C and N deuterated diethylamines (>99 at. % D) were from CDN Isotope Inc. and used as received. Benzene (as solvent), chloroform, ethers, and methanol were of spectroscopic quality (Scharlau, Fluka). Diethyl ether, diisopropyl ether, and tetrahydrofuran were further purified by recondensation under vacuum to remove added stabilizer. Deuterated methanols and deuterated ethers (Glaser AG, Basel, >99.0 at. % D) were used directly. Sulfides (Fluka, >98%) and deuterated dimethyl sulfide (Aldrich, 99.0 at. % D) were used without further purification. Deuterated chloroform was from Glaser AG, Basel (99.8 at. % D). Ammonia was from Multigas (>99.98%, anhydrous).

**Quenching Experiments.** DBO crystals (ca. 0.1 mg), sufficient to maintain the vapor pressure of DBO (0.1 Torr),<sup>20</sup> were placed in a homemade fluorescence cell (volume 50 cm<sup>3</sup>) equipped with a high-vacuum Teflon stopcock. The cell was degassed by freeze–pump–thaw cycles in order to remove oxygen. The fluorescence lifetime of DBO at ambient temperature (295 K) was measured by a commercial laser-flash photolysis setup (Edinburgh Instruments) incorporating a Nd:YAG laser ( $\lambda_{exc} = 355$  nm, fwhm ca. 4 ns, 7 mJ,  $\lambda_{obs} = 430$  nm). The traces were recorded with a digital oscilloscope, with 10 traces accumulated to improve the signal-to-noise ratio, and analyzed by means of least-squares fitting with monoexponential decay functions. The same procedure was applied with quencher, added either as pure liquid (typically 0.5–50  $\mu$ L, transferred with a calibrated GC syringe) or as gas by connecting a lecture bottle to the cell and measuring the pressure with a Hg manometer. Gas-phase concentrations of the quenchers were calculated either with the knowledge of the amount of evaporated liquid amine in the known cell volume or by applying the ideal gas law (for gaseous quenchers), which holds at the low pressures employed (<1 atm). The data reproducibility of the experimental procedures was confirmed through repetitive independent measurements at different concentrations. Special care was taken that all liquid quencher could evaporate by working below its ambient vapor pressure. This restricted the set of quenchers generally to the most volatile ones (bp < 100 °C) and to gases. It should be mentioned that the experimental setup did not allow temperature-dependent studies in the gas phase. Activation energies could therefore not be obtained.

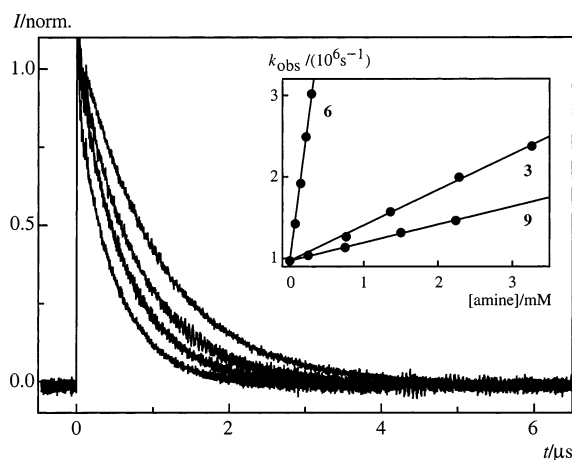
Steady-state fluorescence spectra and UV absorption spectra were recorded with an FLS900 fluorimeter (Edinburgh Instruments) and a Perkin-Elmer Lambda 19 spectrophotometer. A 10-cm cell was employed for the gas-phase absorption spectra.

## Results

**Fluorescence Quenching of DBO in the Gas Phase.** The fluorescence emission of  $n,\pi^*$ -excited DBO in the gas phase is readily observable (Figure 1) and has a reported quantum yield of 0.56.<sup>20</sup> The fluorescence maximum is located at 444 nm.<sup>22</sup> The lifetime in the absence of quenchers was measured as 1030  $\pm$  10 ns at the vapor pressure of DBO (0.1 Torr), cf. Figure 2. This is in agreement with a value reported by Steel and co-workers (ca. 1  $\mu$ s)<sup>20</sup> and somewhat longer than our originally reported value (930 ns).<sup>19,23</sup> The bimolecular quenching rate constants (Table 1) were obtained by plotting the observed



**Figure 1.** Absorption (left) and normalized fluorescence spectra (right) of DBO (a) in the gas phase and (b) in benzene solution.



**Figure 2.** Fluorescence decay traces of DBO in the gas phase ( $\lambda_{obs} = 430$  nm) in the presence of 0, 0.76, 1.36, and 2.28 mM trimethylamine. The inset shows the kinetic quenching plots for diisopropylamine (6), trimethylamine (3), and *n*-propylamine (9).

fluorescence decay rate constants ( $k_{obs}$ ) versus the quencher concentration according to  $k_{obs} = 1/\tau = 1/\tau_0 + k_q[\text{quencher}]$  (inset in Figure 2).

**Quenching by Amines.** The fluorescence quenching rate constants of DBO by amines (1–11) are on the order of  $10^6$ – $10^{10}$  M<sup>-1</sup> s<sup>-1</sup> in the gas phase, with the most inefficient quenching by ammonia and the strongest interaction with secondary amines. The values for all 11 investigated amines are compared in Table 1 with those in benzene solution.<sup>6,7</sup> The gas-phase values are generally higher, by a factor of 10–20, than those in solution. Furthermore, the gas-phase rate constants follow the same dependence on the electron donor ability, that is, ionization potential (IP), as recently reported for benzene solution.<sup>6</sup> Primary amines show the lowest quenching rate constants, while the secondary amines 4–8 quench faster than tertiary amines.

Deuterium isotope effects were investigated for the secondary diethylamine (7). The fully C–D substituted as well as the N–D substituted derivatives were examined. The deuterium isotope effect, which is hardly detectable in the gas phase ( $\leq 10\%$ ), becomes sizable for the N–D derivative in benzene solution (1.3) but remains elusive for the C–D substituted case. This

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**Table 1.** Fluorescence Quenching Rate Constants of DBO in the Gas Phase and in Solution

quencher	IP <sub>a</sub> /eV <sup>a</sup>	$k_q/(10^7 \text{ M}^{-1} \text{ s}^{-1}) [k(\text{H})/k(\text{D})]^b$		$k_{\text{gas}}/k_{\text{soln}}$
		gas phase ( $k_{\text{gas}}$ )	benzene ( $k_{\text{soln}}$ )	
Tertiary Amines				
1 tri- <i>n</i> -propylamine	7.23	89	8.5 <sup>c</sup>	10
2 triethylamine	7.53	64	7.2 [1.8] <sup>c</sup>	9
3 trimethylamine	7.85	43		
Secondary Amines				
4 2,2,6,6-tetramethyl piperidine	7.59	840	40 <sup>c</sup>	21
5 di- <i>n</i> -butylamine	7.69	1900	120 <sup>c</sup>	16
6 diisopropylamine	7.73	680	39 <sup>c</sup>	17
7 diethylamine	8.01	1900	120 <sup>c</sup>	16
<i>d</i> <sub>1</sub> - <i>N</i> -diethyl amine		1800 [1.1]	92 [1.3] <sup>d</sup>	21
<i>d</i> <sub>10</sub> - <i>C</i> -diethyl amine		1900 [1.0]	120 [1.0] <sup>d</sup>	16
8 dimethylamine	8.24	700		
Primary Amines				
9 <i>n</i> -propylamine	8.78	22	2.9 <sup>d</sup>	8
10 methylamine	8.90	7.3		
11 ammonia	10.07	0.64		
Ethers				
12 diisopropyl ether	9.20	3.1	0.07 <sup>d</sup>	44
13 tetrahydrofuran	9.40	2.6 [2.4]	0.2 <sup>d</sup> [5.7] <sup>e,f</sup>	13
14 diethyl ether	9.51	1.6 [2.4]	0.08 <sup>d</sup> [3.9] <sup>e,f</sup>	20
15 dimethyl ether	10.03	1.5		
Sulfides				
16 diethyl sulfide	8.42	260	4.9 <sup>d</sup>	53
17 dimethyl sulfide	8.69	130 [1.3]	6.0 <sup>d</sup> [1.3]	22
Alcohols				
18 methanol	10.84	11	0.18 <sup>e,g</sup>	61
<i>d</i> <sub>1</sub> - <i>O</i> -methanol		4.8 [2.3]	0.02 <sup>e,g</sup> [8.6] <sup>e,f</sup>	240
<i>d</i> <sub>3</sub> - <i>C</i> -methanol		8.8 [1.3]	0.16 <sup>e,g</sup> [1.1] <sup>e,f</sup>	55
<i>d</i> <sub>4</sub> -methanol		4.0 [2.8]	0.009 <sup>e,g</sup> [20.6] <sup>e,f</sup>	450
Haloalkanes				
19 chloroform	11.37	17 [7.7]	0.61 <sup>e,g</sup> [9.4] <sup>e,f</sup>	28

<sup>a</sup> Adiabatic ionization potentials from ref 56. <sup>b</sup> Bimolecular fluorescence quenching rate constants, 10% error; isotope effects are given in square brackets. <sup>c</sup> Reference 6. <sup>d</sup> This work in benzene. <sup>e</sup> Obtained by using the revised value for  $\tau_0$  (1030 ns, this work) and the fluorescence lifetimes from refs 19, 23, and 27, except for *d*<sub>8</sub>-tetrahydrofuran (191 ns, this work), diethyl ether (123 ns, this work), and *d*<sub>10</sub>-diethyl ether (362 ns, this work). <sup>f</sup> Isotope effect refers to neat quencher. <sup>g</sup> Rate constant refers to neat quencher.

result, as well as the much higher reactivity of secondary amines compared to tertiary ones, points to a marked participation of the N–H rather than the C–H bonds in the quenching. This has been deduced previously.<sup>6,24</sup> Note that quenching by exciplex formation or C–H hydrogen abstraction (see also a later discussion) should both increase with decreasing IP,<sup>5</sup> that is, should be faster for tertiary amines, unless an additional quenching mechanism competes (in this case N–H abstraction from secondary amines).

The insignificant deuterium isotope effect in the gas phase even for N–H/N–D in diethylamine is most likely due to the high reactivity, which is known to significantly reduce or even eradicate isotope effects.<sup>25</sup> Although the rate constants for the secondary amines fall 1 order of magnitude below the encounter rate constant,<sup>26</sup> the well-defined geometry of the interaction (exciplex formation<sup>7,9</sup> or hydrogen-transfer transition state<sup>23,27,28</sup>)

may impose a large entropic factor on the reaction rate. It is therefore conceivable that the rate constants measured for the secondary amines are the maximum values expected for this reaction type, as can be alternatively deduced from the fact that the quenching rate constant is leveling off upon going from diethylamine to di-*n*-butylamine. In general, one expects a quencher with a lower IP (di-*n*-butylamine) to react faster than one with a higher IP (diethylamine).<sup>5</sup> The small deuterium isotope effect for the secondary amines can therefore be related to the fast quenching kinetics, which is near the reaction rate limit. Large deuterium isotope effects in the gas phase were observed, however, for less efficient quenchers such as alcohols and chloroform (Table 1).

Note also that 2,2,6,6-tetramethylpiperidine (**4**), diisopropylamine (**6**), and dimethylamine (**8**) react significantly slower than di-*n*-butylamine (**5**) and diethylamine (**7**). We presume that amine **8** reacts slower than **5** and **7** because of its higher IP while **4** and **6** may show a steric effect of the alkyl groups on the N–H abstraction process.

#### Quenching by Other Heteroatom-Containing Quenchers.

To compare the reactivity of the amines with less potent electron donors (quenchers with higher IP), ethers, alcohols, and sulfides were included in the study. These data are also shown in Table 1. Ethers (**12–15**) and alcohols (**18**) quench the fluorescence of DBO in the gas phase with rate constants of  $10^7$ – $10^8 \text{ M}^{-1} \text{ s}^{-1}$ , with methanol being the most efficient quencher. The values are again 10–60-fold increased compared to those in solution. Furthermore,  $\alpha$  C–H deuterium isotope effects of  $k(\text{H})/k(\text{D}) \approx 2$ – $3$  were observed (Table 1). These are lower than those obtained for quenching in neat liquid ethers, that is, 3.9 for diethyl ether and 5.7 for tetrahydrofuran. Methanol shows a higher deuterium isotope effect for the O–H (2.3) than for the C–H bond (1.3), in support of the previously recognized preference for O–H abstraction.<sup>24,27</sup> Surprisingly, sulfides (**16** and **17**) quenched with unexpectedly high rate constants above  $10^9 \text{ M}^{-1} \text{ s}^{-1}$ , resulting in a different selectivity toward the quencher type in the gas phase and in solution; that is, tertiary amines quench faster than sulfides in solution but are slower in the gas phase. The deuterium isotope effect for **17** was 1.3, the same as that obtained for quenching in benzene solution. Chloroform (**19**) was also included, because it shows a fully manifested deuterium isotope effect in solution.<sup>23</sup> The isotope effect in the gas phase falls somewhat short of the solution value (7.7 versus 9.4) but is nevertheless the largest measured in this gas-phase series.

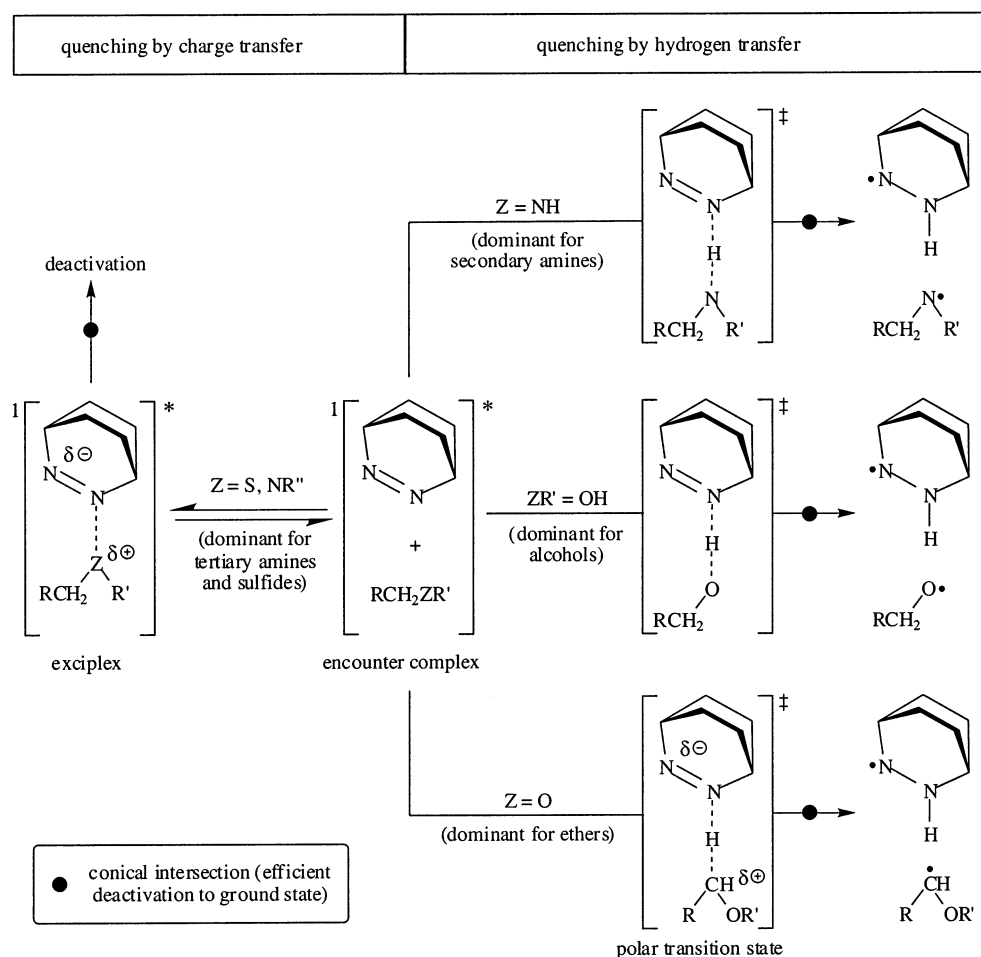
#### Discussion

The present study compares the intermolecular photoreactivity of the  $n,\pi^*$ -excited azoalkane 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO) in the gas phase with that in benzene solution. Although the study of simple photoreactions in the gas phase, in this case hydrogen abstraction and exciplex formation of  $n,\pi^*$ -excited states, is a matter of fundamental interest, there are at least three additional specific motivations. (1) Theoretical descriptions of

- (26) A collision frequency of  $3 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$  was calculated from the sphere collision model (cf. Levine, I. N. *Physical Chemistry*; McGraw-Hill, Inc.: New York, 1995; p 442.). DBO ( $r = 3.07 \text{ \AA}$ , cf. ref 8) and diethylamine ( $r = 3.44 \text{ \AA}$ , calculated, this work) were used as representative reactants.  
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Scheme 1



these quenching mechanisms by high-level *ab initio* calculations, which have recently been reported,<sup>8,9,28,29</sup> refer to the gas phase. (2) Discussions of structural and electronic effects on photochemical reaction mechanisms depend on measures of bond dissociation energy and electron donor properties of the quenchers; these are more generally and accurately accessible for the gas phase (cf. ionization potentials) than in the particular solvent under investigation. (3) A comprehensive understanding of solvent effects on photoreactivity requires the gas-phase reactivity as a reference point.

The structure of the Discussion will be such that we will first focus on the similarities in photoreactivity of DBO in the gas phase and in solution and then turn to some contrasts with respect to the absolute and relative reactivity. Last, the results for DBO will be compared with previous results for triplet ketones to allow generalizations for  $n, \pi^*$ -excited states and to recognize differences in the behavior of azoalkanes and ketones.

**Similarities of Photoreactivity in the Gas Phase.** The photoreactivity of the  $n, \pi^*$ -singlet-excited azoalkane DBO has been subject to several recent studies.<sup>6–10,19,23–25,27,28</sup> On the basis of solution measurements and *ab initio* calculations, we have previously assigned the following predominant reaction mechanisms (Scheme 1): exciplex formation for tertiary amines and sulfides,<sup>6–10</sup> N–H hydrogen abstraction for primary and secondary amines,<sup>6,24</sup> O–H hydrogen abstraction for alco-

hols,<sup>19,27</sup> and C–H hydrogen abstraction for ethers and chloroform.<sup>9,19,23,24</sup>  $\alpha$  C–H abstraction may compete for primary and tertiary amines as well as sulfides, but it appears unlikely for secondary amines, because secondary amines lacking  $\alpha$  hydrogens (**4**) react at comparable rate constants as those containing  $\alpha$  hydrogens (**6**). The quantum yields for the formation of photoproducts are low, however, in the quenching of  $n, \pi^*$ -singlet-excited states.<sup>5,7,8,10,19,23,25,27,30–32</sup> This is due to the occurrence of a conical intersection along each reaction path (bold points in Scheme 1),<sup>9,23,27,28</sup> where efficient deactivation to the ground-state reactants occurs.

It must be emphasized that the exciplex with tertiary amines and sulfides is not simply an excited encounter complex which is loosely bound through weak intermolecular interactions. The exciplex has in fact a well-defined constitution (Scheme 1) in which a significant amount of CT occurs through the formation of a three-electron–two-center bond between one azo nitrogen and the heteroatom of the quencher.<sup>7–9</sup> This tight geometry of the exciplex,<sup>7</sup> which differs dramatically from the transition-state geometry required for hydrogen abstraction (also shown in Scheme 1),<sup>23,27</sup> has recently led us to disregard exciplex-mediated hydrogen abstraction as a mechanistic alternative for  $n, \pi^*$ -excited states and aliphatic quenchers.<sup>5</sup> In other words,

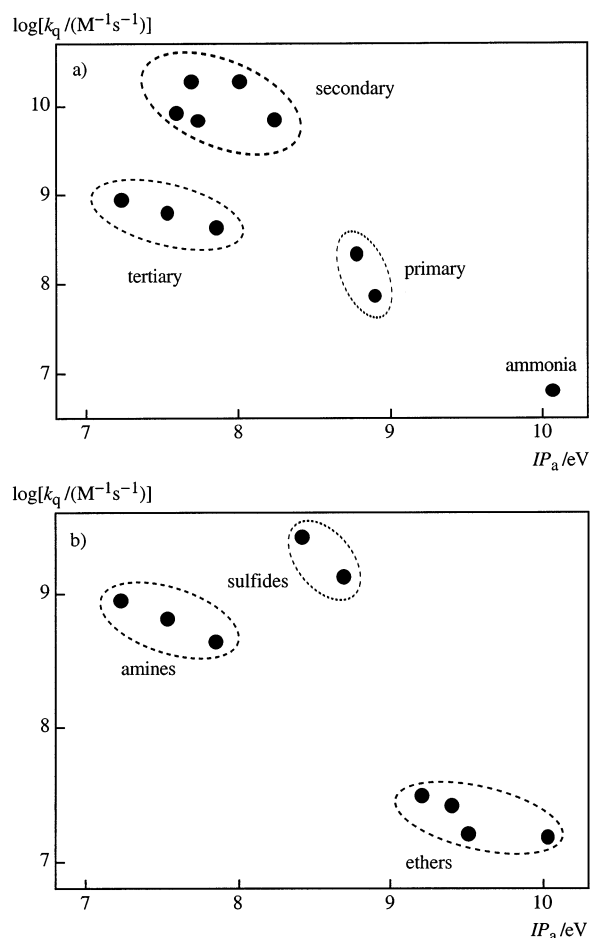
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**Figure 3.** Plots of the gas-phase quenching rate constants ( $\log k_q$ ) versus the adiabatic ionization potentials ( $IP_a$ ) (a) for tertiary, secondary, and primary amines, as well as ammonia, and (b) for tertiary amines, dialkyl sulfides, and ethers.

we have no indication for hydrogen abstraction following exciplex formation.

Evidence for a dramatic change in the reaction mechanism upon going from solution to the gas phase was not obtained. The situation for the investigated amines **1–11** is reminiscent of that in benzene solution.<sup>6</sup> There is a rather qualitative correlation with the ionization potential for tertiary amines, suggesting a certain amount of CT in the gas phase as well, but secondary amines clearly stand out in that they quench much faster than expected from their intermediate IP values (Figure 3a). The underlying reasons for this peculiar behavior were recently ascribed to a competitive N–H abstraction, which is favored by the strongly exothermic reaction thermodynamics for azoalkanes, the less electrophilic character of  $n,\pi^*$ -excited azoalkanes compared to ketones, and the low antibonding character in the transition state for hydrogen transfer between heteroatom centers.<sup>33</sup>

(33) The antibonding derives from the fact that the energy of a three-center transition state ( $X\cdots H\cdots Y$ ) for hydrogen abstraction is also dependent on the X–Y bond strength; N–N bonds are much weaker than C–N bonds, thereby causing decreased antibonding in the transition state, which accelerates the reaction, e.g., hydrogen abstraction from N–H relative to C–H. This effect has been discussed for photoinduced hydrogen abstraction reactions in ref 24 and is well established for hydrogen abstractions by radicals, cf. Zavitsas, A. A.; Chatgililoglu, C. *J. Am. Chem. Soc.* **1995**, *117*, 10645–10654.

The large deuterium isotope effects observed for alcohols, ethers, and chloroform in the gas phase provide strong support for hydrogen atom transfer as quenching mechanism in these cases. The fact that the isotope effects in solution are fully developed for methanol and chloroform demonstrates further that alternative quenching mechanisms such as exciplex-induced quenching do not compete for these quenchers. In fact, high-level quantum-chemical calculations (gas phase) have revealed no exciplex minimum in the case of ethers as quenchers of singlet-excited DBO.<sup>9</sup> The deuterium isotope effects in the gas phase, however, are significantly smaller than in solution, which may be in part related to the increased reactivity and concomitant lower selectivity in the gas phase. Besides the absolute reactivity, the specific type of quencher must play an important role in determining the actual isotope effect because chloroform has a very similar rate constant as methanol, but its isotope effect is nearly fully developed in the gas phase (Table 1). Note again that for methanol, where two different types of hydrogens are available, the isotope effect is larger for O–D than for C–D (2.3 versus 1.3). This, along with the larger absolute rate constants for alcohols, for example,  $1.1 \times 10^8 M^{-1} s^{-1}$  for methanol versus  $1.5 \times 10^7 M^{-1} s^{-1}$  for dimethyl ether, confirms the preferential abstraction of the electrophilic O–H hydrogen.<sup>24,27</sup> The underlying reasons for this preferential abstraction of the more strongly bound hydroxyl hydrogen (as opposed to the more weakly bound C–H) are the same as those responsible for a preferential N–H abstraction in the case of secondary amines (see previous discussion).<sup>24</sup> The present gas-phase study reveals that the increased reactivity of excited azoalkanes toward electrophilic hydrogens (O–H and N–H) is a truly intrinsic property of the chromophore and not a consequence of solvation effects.

Interestingly, the data suggest a significant dependence on IP in the quenching process not only for amines but also for the ethers **12–15** (Table 1, Figure 3b). The correlation improves further if one normalizes the gas-phase rate constants by the number of abstractable  $\alpha$  C–H hydrogens.<sup>34</sup> Evidently, ethers with lower IP are the better quenchers. This is a nontrivial finding because ethers are presumed (and have been calculated)<sup>9,30</sup> to react via hydrogen abstraction rather than CT (exciplex formation). Because the  $\alpha$  C–H bond dissociation energies are very similar ( $93 \pm 1 \text{ kcal mol}^{-1}$ ),<sup>35–37</sup> the ionization potential must affect the hydrogen abstraction process in a different manner.

The importance of the electron donor strength of the substrate in hydrogen atom transfer reactions has just recently been emphasized for amines with cumyloxyl radicals and triplet acetone as abstracting species.<sup>5</sup> It was tentatively suggested, akin to previous suggestions for radical reactions,<sup>38,39</sup> that a polar transition state effect is operative in the hydrogen abstraction from amines, and this argument may apply for ethers as well. An abstracting electron-deficient alkoxy radical or  $n,\pi^*$ -excited

(34) Note that a stereoelectronic effect for diisopropyl ether, which has been postulated in the reaction with *t*-butoxyl radicals (cf. Malatesta, V.; Scaiano, J. C. *J. Org. Chem.* **1982**, *47*, 1455–1459), was not observed in the present study.

(35) Brocks, J. J.; Beckhaus, H.-D.; Beckwith, A. L. J.; Rüchardt, C. *J. Org. Chem.* **1998**, *63*, 1935–1943.

(36) Shtarev, A. B.; Tian, F.; Dolbier, W. R., Jr.; Smart, B. E. *J. Am. Chem. Soc.* **1999**, *121*, 7335–7341.

(37) Laarhoven, L. J. J.; Mulder, P.; Wayner, D. D. M. *Acc. Chem. Res.* **1999**, *32*, 342–349.

(38) Zavitsas, A. A.; Pinto, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 7390–7396.

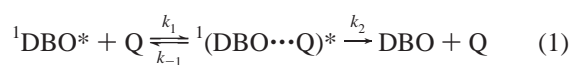
(39) Encina, M. V.; Diaz, S.; Lissi, E. *Int. J. Chem. Kinet.* **1981**, *13*, 119–123.

state (ketone or azoalkane) may polarize the transition state (e.g., as explicitly shown for ethers in Scheme 1). The resulting positive partial charge on the carbon center may be strongly dependent on electron donation from the adjacent oxygen (for ethers) or nitrogen (for amines) lone pairs. Hydrogen abstraction may therefore depend on the ionization potential even in the absence of exciplex formation. In this context, it should again be emphasized that hydrogen abstraction is unlikely to occur as a follow-up reaction from an exciplex with ethers or alcohols. In fact, an exciplex minimum has not been located with these poorly electron-donating quenchers,<sup>9</sup> and this type of “exciplex-mediated” hydrogen abstraction appears to be in general disfavored for aliphatic hydrogen donors because of the very different geometry of the exciplex and the hydrogen transfer transition state (Scheme 1).<sup>5</sup>

**Variations in Photoreactivity in the Gas Phase.** The subsequent discussion will be focused on absolute and relative variations in the photoreactivity in solution and in the gas phase. First of all, the marked increase in the photoreactivity in the gas phase stands out and requires immediate attention. Faster rate constants in the gas phase are, of course, expected for reactions which are limited by diffusion in solution, but they are not a priori evident for slower reactions, whose reaction rates are determined by enthalpic effects.

Two enthalpic effects are deemed responsible for the increased rates of fluorescence quenching of DBO in the gas phase. First, there is a small difference in the singlet excitation energies of DBO in the gas phase as extracted from the 0–0 fluorescence bands (Figure 1). One obtains an excitation energy of 3.29 eV in the gas phase and 3.23 eV in benzene solution. However, the observed rate enhancements and, in particular, the variations for different types of quenchers, cannot be entirely due to this constant enthalpic aspect. Previous studies of solvent effects have demonstrated that, although the absorption and emission spectra show small and systematic shifts with the solvent polarizability,<sup>22</sup> it is the polarity of the solvent which dominates the photochemical reactivity of DBO.<sup>8</sup> This becomes particularly obvious if one compares the fluorescence quenching rate constants of DBO by triethylamine. These are higher in *n*-hexane than in acetonitrile, that is, two solvents with similar polarizability<sup>22</sup> but largely different polarity.<sup>8</sup> A more detailed understanding of the reactivity in the gas phase therefore requires a more evolved analysis of the relationship between kinetics, solvation energies, solvent polarity, and quencher properties.

We will first analyze the rate enhancement for amines as quenchers where exciplexes are the presumed intermediates. The arguments will be shown to be transferable to the case of hydrogen donors as quenchers. The kinetic scheme for the formation and decay of the exciplex can be described by assumption of the *preequilibrium and steady-state* situation in eq 1 ( $k_{-1} \gg k_1[Q] \cup k_2$ ),<sup>7</sup> for which the bimolecular quenching rate constant is given by eq 2.



$$k_q \approx k_2 K \text{ with } K = k_1/k_{-1} \quad (2)$$

Both a shift of the equilibrium to the exciplex ( $K$ ) and a faster decay of the latter ( $k_2$ ) increase the observed bimolecular quenching rate constant. These thermodynamic and kinetic

parameters are dependent on the reaction medium and on the molecular properties of the system, that is, reactants and intermediates, as will now be discussed.

$$\Delta G_{\text{solvent}} = \frac{N_A}{4\pi\epsilon_0} \left( \frac{\mu_{\text{DBO}}^2}{r_{\text{DBO}}^3} + \frac{\mu_{\text{Q}}^2}{r_{\text{Q}}^2} - \frac{\mu_{\text{DBO-Q}}^2}{r_{\text{DBO-Q}}^3} \right) \times \left( \frac{\epsilon - 1}{2\epsilon + 1} \right) = C \times \left( \frac{\epsilon - 1}{2\epsilon + 1} \right) \quad (3)$$

The polarity dependence of the free energy for exciplex formation can be approximated by the Kirkwood–Onsager continuum model (eq 3 with  $\mu$  being dipole moments and  $r$  molecular radii).<sup>40,41</sup> For the quenching of  $n,\pi^*$ -excited states by electron donors, it was recently demonstrated that the sign of the structural constant  $C$  determines whether the system shows a normal or an “inverted” solvent effect.<sup>8</sup> For DBO-amine/sulfide systems,  $C$  is positive because of the dipolar stabilization of the reactants (in particular the strongly dipolar DBO) relative to the reactive complex (in this case exciplexes with partial CT character). This results in an acceleration of the quenching in media of lower polarity. In other words, the equilibrium constant  $K$  for the formation of the exciplex is increased in nonpolar environments. Note that the opposite applies for stronger electron-accepting ketones (see later).<sup>8</sup>

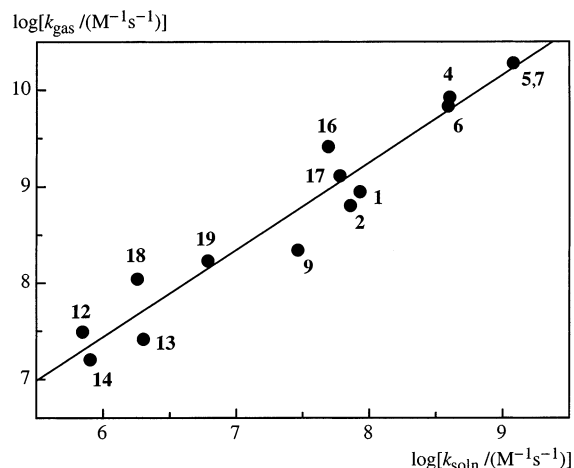
In the gas phase as the most nonpolar medium, the solvent polarity term vanishes with the consequence that the “inverted” solvent effect is expected to manifest itself strongest (highest rate constants). This is in agreement with the data for amines in Table 1. In fact, from the functional dependence on the  $(\epsilon - 1)/(2\epsilon + 1)$  term, it follows that one expects a large effect between the gas phase ( $\epsilon = 1.00$ ) and a relatively nonpolar solvent like benzene ( $\epsilon = 2.40$ ).<sup>42</sup> The observed order of magnitude difference in the rate constants between benzene solution and the gas phase is therefore not unexpected. Note that the overall variation between the gas phase and benzene solution by 1 order of magnitude is about the same as that between a very nonpolar and polar solvent.<sup>8</sup>

The simple arguments derived from the Kirkwood–Onsager model can be similarly applied to hydrogen donors as quenchers. The role of the exciplex in eq 1 is then replaced by that of the transition state for hydrogen transfer, and instead of the free energy for exciplex formation in eq 3 (which enters the observed rate constant through the equilibrium constant in eq 2), a free energy of activation (for hydrogen transfer) is calculated. An acceleration of the reaction in less polar media then applies whenever at least one strongly dipolar reactant is involved and when the dipole moment of the reactive complex or transition state is not significantly increased compared to the reactants. For hydrogen atom abstractions, it is reasonable to assume that this transition state has little CT character (less than in an exciplex), such that a similar or more pronounced outcome as for amine quenching should apply, that is, a positive  $C$  and an inverted solvent effect. This conclusion is supported by the experimental data in Table 1, which do in fact reveal an increase in the quenching rate constant in the gas phase for all

(40) Kirkwood, J. G. *J. Chem. Phys.* **1934**, *2*, 351–361.

(41) Onsager, L. *J. Am. Chem. Soc.* **1936**, *58*, 1486–1493.

(42) Laurence, C.; Nicolet, P.; Dalati, M. T.; Abboud, J.-L. M.; Notario, R. *J. Phys. Chem.* **1994**, *98*, 5807–5816.



**Figure 4.** Double-logarithmic plot of the gas-phase versus solution quenching rate constants.

investigated quenchers, regardless of the quenching mechanism (exciplex formation, O–H, N–H, or C–H abstraction).

With respect to the relative reactivity toward different quenchers, that is, selectivity, in the gas phase versus solution, a direct correlation (Figure 4;  $\log k_{\text{gas}} = 2.00 + 0.906 \log k_{\text{soln}}$ ,  $r = 0.970$ ,  $n = 13$ ) shows an overall satisfactory agreement. However, a closer inspection of the  $k_{\text{gas}}/k_{\text{soln}}$  ratios in Table 1 reveals subtle but systematic variations, which are responsible for the deviations from the regression line in Figure 4. In particular, one notes that the increase in reactivity upon going from solution to the gas phase is particularly large for those quenchers which quench DBO preferentially through the transfer of electrophilic N–H and O–H hydrogen atoms. Secondary amines with abstractable N–H hydrogens show a larger differentiation ( $k_{\text{gas}}/k_{\text{soln}} \approx 20$ ) than tertiary amines (ca. 10), and alcohols with abstractable O–H hydrogens show a larger effect (ca. 60) than ethers (<45). Strikingly, the ratio of  $k_{\text{gas}}/k_{\text{soln}}$  reaches values close to 500 for the O deuterated methanols. This is the largest discrepancy in absolute reactivity between gas phase and solution observed in this study. Obviously, the reactivity of N–H and in particular O–H shows a larger decrease in solution than the reactivity of C–H bonds. This finding is of great importance. We presume that the bond polarity, which decreases in the order O–H > N–H > C–H, is important. We suggest tentatively that the more dipolar O–H and N–H bonds are better solvated because of enhanced dipole/dipole or dipole/induced dipole interactions and therefore less reactive in solution relative to the gas phase. In essence, it appears that O–H and N–H bonds are better “protected” by the solvent. Related arguments have been advanced to account for the reduced tendency of phenol O–H bonds to undergo hydrogen abstraction in protic versus nonprotic solvents.<sup>32,43</sup> In this case, hydrogen bonding was assumed to reduce the reactivity.

Interestingly, one expects a priori no response of the solvent effect ( $k_{\text{gas}}/k_{\text{soln}}$ ) to deuteration of the quencher. The circumstance that such a dependence is nevertheless obtained (cf. methanol series) may be a reflection that the rate constants in the gas phase lie close to the upper limit. This is suggested by the

decreased deuterium isotope effects for methanol in the gas phase.

Sulfides, whose quenching rate constants are expected to lie between amines and ethers on the basis of their intermediate ionization potentials, quench exceptionally fast in the gas phase (Figure 3b). In fact, a “switch-over” in relative reactivity between sulfides and tertiary amines is observed. In solution, the sulfides are the less efficient quenchers, and we have previously argued that this reactivity order is in line with the higher IP and the related expectations for an exciplex-induced quenching.<sup>8</sup> CT-induced quenching by sulfides has been previously proposed for excited ketones.<sup>44,45</sup> However, the present gas-phase data demonstrate that the sulfides are more potent quenchers (factor 2–4) than the corresponding tertiary amines in the gas phase, cf. rate constants of  $1.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  versus  $4.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  for dimethyl sulfide versus trimethylamine. In addition, because the C–H bond dissociation energy in dimethyl sulfide is somewhat higher than in tertiary amines and similar to that in ethers (cf. values of  $93.4 \text{ kcal mol}^{-1}$  for dimethyl sulfide,<sup>46</sup>  $92.4 \text{ kcal mol}^{-1}$  for trimethylamine,<sup>47</sup> and  $93.4 \text{ kcal mol}^{-1}$  for dimethyl ether<sup>36</sup>), a different propensity toward hydrogen abstraction cannot be the cause for the more efficient gas-phase quenching of sulfides either (hydrogen abstraction must take place to some degree, however, as revealed by the deuterium isotope effect for 17).

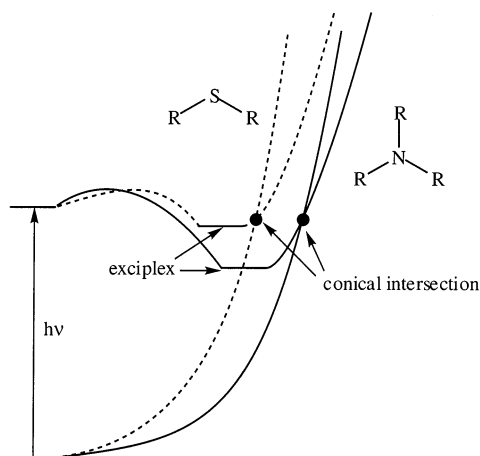
We suggest tentatively that the very efficient quenching of the sulfides in the gas phase is due to a faster deactivation of the intermediary exciplex ( $k_2$  in eq 1). The deactivation rate constant of the exciplex is primarily dependent on the precise topology of the excited-state hypersurface in the vicinity of the exciplex and in particular on the geometric displacement and energetic activation required to reach the conical intersection with the ground-state surface where radiationless deactivation occurs.<sup>9</sup> This topology is expected to be strongly dependent on the nature of the quencher (recall that a three-electron–two-center CT bond stabilizes the exciplex)<sup>7</sup> such that the effects on the exciplex deactivation rate constant ( $k_2$ ) may not be predictable in a straightforward manner on the basis of ionization energies alone. One could imagine the scenario in Figure 5, where the exciplex of the sulfide may be somewhat destabilized relative to the amine exciplex in the gas phase (smaller  $K$  in eq 1), but where the conical intersection, which triggers exciplex deactivation, is more readily accessible in the sulfide case (larger  $k_2$ ).<sup>48</sup>

Note also that the quenching rate constants for triethylamine reveal a decrease by a factor of ca. 9 upon going from the gas phase to benzene, but a factor of ca. 20–40 for sulfides (Table 1). The fact that the reactivity of the sulfides in solution shows a more pronounced decrease than for tertiary amines (for which the same quenching mechanism applies) results in the observed switch-over in their relative reactivity. The Kirkwood–Onsager model can account for the larger solvent effect of sulfides, if

- (44) Guttenplan, J. B.; Cohen, S. G. *J. Org. Chem.* **1973**, *38*, 2001–2007.  
 (45) Inbar, S.; Linschitz, H.; Cohen, S. G. *J. Am. Chem. Soc.* **1982**, *104*, 1679–1682.  
 (46) This value was calculated with the G2(MP2) method, which is known to reproduce experimental data within an accuracy of  $1 \text{ kcal mol}^{-1}$ , cf. Turecek, F. *J. Phys. Chem.* **1994**, *98*, 3701–3706.  
 (47) Wayner, D. D. M.; Clark, K. B.; Rauk, A.; Yu, D.; Armstrong, D. A. *J. Am. Chem. Soc.* **1997**, *119*, 8925–8932.  
 (48) Preliminary ab initio calculations at the CAS-SCF level of theory confirm a similar quenching mechanism for sulfides as for amines (ref 9), including the presence of an exciplex intermediate and a proximate conical intersection. Sinicropi, A.; Olivucci, M. Personal communication.

(43) Evans, C.; Scaiano, J. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1992**, *114*, 4589–4593.





**Figure 5.** Possible topology for the exciplex-induced quenching of singlet-excited DBO by sulfides (---) and tertiary amines (—) in the gas phase. Shown are the ground- and excited-state energy hypersurfaces and the location of the conical intersection relative to the exciplex.

one assumes that the solvent stabilization of the reactants relative to the exciplex is more pronounced for the sulfides than for the tertiary amines. For example, sulfides as reactants are expected to experience a stronger solvent stabilization relative to tertiary amines because of their higher dipole moment, for example,  $\mu = 1.50$  D for dimethyl sulfide<sup>49</sup> and  $\mu = 0.86$  D for triethylamine.<sup>50</sup>

**Comparison with  $n,\pi^*$ -Excited Ketones.** As mentioned in the Introduction, benzophenone is the most comprehensively studied  $n,\pi^*$ -excited ketone, but its low vapor pressure requires elevated temperatures (ca. 400 K) in gas-phase studies,<sup>15,16,18</sup> which greatly complicates a direct comparison with the ubiquitous ambient-temperature solution data in terms of absolute rates and selectivity. In particular, higher temperatures may favor different reaction pathways.

Some gas-phase studies for other ketones such as acetone, biacetyl, and acetophenone have also become available.<sup>12–14,17,51</sup> Scaiano and co-workers investigated the triplet quenching of acetone and biacetyl by four secondary and tertiary aliphatic amines on the basis of competitive product studies or phosphorescence measurements.<sup>12</sup> They observed a drop in reactivity by about 1 order of magnitude in the gas phase compared to solution and a different selectivity toward the different quenchers, namely a larger reactivity of secondary relative to tertiary amines in the gas phase. They concluded that hydrogen abstraction is dominant in the gas phase. We have recently concluded that the quenching of triplet acetone by amines in solution can be adequately accounted for by considering only hydrogen abstraction, and that exciplex formation competes only for singlet-excited acetone.<sup>5</sup> The different selectivity of triplet acetone in the gas phase and in solution must therefore be attributed to a different response of different types of abstractable hydrogens toward solvation.

(49) Weast, R. C.; Lide, D. R.; Astle, M. J.; Beyer, W. H. *CRC Handbook of Chemistry and Physics*; CRC Press: Boca Raton, FL, 1990.

(50) Ivanov, M. G.; Zhuravlev, E. Z.; Dergunov, Y. I.; Elizarova, T. P. *Zh. Obshch. Khim.* **1990**, *60*, 1209–1212.

(51) It should be kept in mind that the differences in the excitation energies in the gas phase and in solution, which are precisely known for DBO (Figure 1), are not accurately known for these triplet ketones (compare, for example, the results reported in Lin, Z.-P.; Aue, W. A. *Spectrochim. Acta A* **1999**, *56*, 111–117, with those in Cebul, F. A.; Kirk, K. A.; Lupo, D. W.; Pittenger, L. M.; Schuh, M. D.; Williams, I. R.; Winston, G. C. *J. Am. Chem. Soc.* **1980**, *102*, 5656–5661). This presents an uncertainty in the interpretation of the gas-phase reactivity of triplet ketones.

The arguments developed for singlet-excited DBO in the present study can now be transferred to triplet acetone. First, the reduced reactivity in the gas phase is related to the fact that excited acetone is significantly less dipolar than DBO.<sup>5</sup> This gives rise to the expectation of a regular solvent effect. This effect is not experimentally manifested in different solvents<sup>5,52</sup> but may well become detectable upon going from solution to the gas phase, where the largest variation in solvation energy applies (cf.  $(\epsilon - 1)/(2\epsilon + 1)$  term in eq 3). Second, the increased reactivity of secondary amines can be accounted for in terms of a more pronounced increase in reactivity of N–H versus C–H hydrogens in the gas phase versus solution (see previous discussion of  $k_{\text{gas}}/k_{\text{soln}}$  ratios). The gas-phase data indicate that N–H abstraction is inherently favored even for ketones, as expected from a reduced antibonding character in the transition state.<sup>33</sup> It appears therefore that solvent effects mask the inherently higher reactivity of N–H bonds, either completely (for ketones), or partly (for DBO). The kinetic data for triplet ketones are therefore in agreement with our notion (see previous discussion) that O–H and N–H bonds are better “protected” by the solvent.

Triplet acetophenone was studied by Steel and co-workers and later by Matsushita et al.<sup>13,17</sup> A correlation of the quenching rate with the ionization potentials of 13 amines also supported a CT mechanism in the gas phase<sup>16,17</sup> with the presumed involvement of an exciplex with moderate CT.<sup>53</sup> Acetophenone and other  $n,\pi^*$ -excited aromatic ketones are stronger electron acceptors than DBO.<sup>54</sup> A large degree of CT in the exciplex, an increased exciplex dipole moment, and, thus, a regular solvent effect are expected for aromatic ketones. This is also in agreement with the strongly negative  $C$  value ( $C = -0.466$  D<sup>2</sup> Å<sup>-3</sup>) calculated for benzophenone.<sup>8</sup> The available data for quenching of triplet acetophenone by triethylamine,<sup>13</sup>  $k_{\text{q}} = 2.3 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup> in the gas phase and  $k_{\text{q}} = 3.8 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup> in acetonitrile solution, support the expected regular solvent effect, which can be rationalized once more through the Kirkwood–Onsager model (eq 3).

Strikingly, the fastest quenching of triplet acetophenone was observed for secondary amines,<sup>17</sup> although tertiary amines are the better electron donors. This has led the authors to the conclusion that it is not the photoreactivity of secondary amines which is surprisingly high in the gas phase, but that the photoreactivity of tertiary amines is unexpectedly low because of a steric effect. Building upon this assumption, the authors implied an increased proportion of CT in the quenching process in the gas phase (on the basis of a correlation of the quenching rate constants *excluding* the tertiary amines).<sup>17</sup> The present study of DBO fluorescence quenching in the gas phase allows an

(52) Yip, R. W.; Loutfy, R. O.; Chow, Y. L.; Magdzinski, L. K. *Can. J. Chem.* **1972**, *50*, 3426–3431.

(53) The activation energy for the gas-phase quenching of acetophenone by triethylamine is negative ( $E_{\text{a}} = -1.0$  kcal mol<sup>-1</sup>, cf. ref 13), consistent with an exciplex preequilibrium (cf. ref 5). In solution, a positive activation energy ( $E_{\text{a}} = +1.5$  kcal mol<sup>-1</sup>) was observed (ref 13), which is in agreement with a full electron transfer.

(54) The driving force for electron transfer ( $\Delta G_{\text{et}}$ ) in the gas phase can be calculated as  $\Delta G_{\text{et}} = \text{IP} - \text{EA} - E^* - C$ , with EA being the gas-phase electron affinity. Triplet-excited acetophenone (EA = 2.06 eV; cf. Cumming, J. B.; Kebarle, P. *J. Am. Chem. Soc.* **1977**, *99*, 5818–5820.  $E^* = 3.15$  eV; cf. Lin, Z.-P.; Aue, W. A. *Spectrochim. Acta A* **1999**, *56*, 111–117.) shows a slightly endergonic thermodynamics ( $\Delta G_{\text{et}} = +0.26$  eV) in the reaction with triethylamine (IP = 7.53 eV), while for singlet-excited DBO (EA = -0.50 eV; Allan, M. Personal communication.  $E^* = 3.29$  eV) a strongly endergonic thermodynamics results ( $\Delta G_{\text{et}} = +2.68$  eV). The Coulomb term  $C = e^2/4\pi\epsilon_0 r$  was taken as 2.06 eV ( $r = 7$  Å).



alternative understanding of the effects observed for triplet acetophenone. Accordingly, the stronger increase in reactivity of secondary amines in the gas phase (as opposed to the weaker increase for tertiary amines) is presumably a consequence of a different selectivity, namely a preferential abstraction of the N–H hydrogens of secondary amines in the gas phase; in solution, the reactivity of N–H hydrogens is reduced and competes less effectively. A steric effect for tertiary amines as previously implied is not indicated. In fact, we have recently demonstrated that steric and stereoelectronic hindrance effects for tertiary amines become operative only with three secondary alkyl substituents<sup>7</sup> and some bicyclic ones such as DABCO.<sup>7,55</sup>

### Conclusions

The present comparative study on photoreactivity in the gas phase and in solution appears to be the most comprehensive one available with respect to the variation of the quencher type as well as the number of quenchers and deuterium isotope effects examined. The gas-phase data for fluorescence quenching of DBO by amines, sulfides, and other heteroatom-containing quenchers, as well as their comparison with the previous data for acetone and acetophenone, allow two principal conclusions.

(55) Griller, D.; Howard, J. A.; Marriott, P. R.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 619–623.

(56) Linstrom, P. J.; Mallard, W. G. *NIST Chemistry WebBook*; NIST Standard Reference Database No. 69; National Institute of Standards and Technology: Gaithersburg, MD, 2001.

(1) The reactivity of O–H and N–H bonds in photoinduced hydrogen abstraction reactions shows a larger decrease upon changing from the gas phase to solution than the reactivity of C–H bonds. This can be related to a better solvation and therefore “protection” of the strongly dipolar O–H and N–H bonds. (2) The absolute photoreactivity in the gas phase may vary in dependence on the reactants. Excited states and quenchers with high dipole moments may give rise to higher quenching rate constants in the gas phase than in solution. The latter is a pronounced manifestation of the previously described “inverted” solvent effect,<sup>8</sup> which can be understood, like the regular solvent effect, through the simple Kirkwood–Onsager continuum model. In addition to these two conclusions, the surprisingly high quenching rate constants for sulfides in the gas phase stand out, which are unexpected from their moderate ionization potentials. This kinetic effect is presumably related to a fast nonradiative deactivation of the sulfide-excipient triggered by a very close-lying conical intersection.

**Acknowledgment.** Dedicated to Prof. J. Wirz on the occasion of his 60th birthday. The authors thank the Swiss National Science Foundation for support through Project 620-58000 for W.M.N. and support for D.K. during his research visit in Basel. This work was also supported by the Fonds der Chemischen Industrie (Kekulé fellowship for U.P.).

JA020400H