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Dual Pathways for the Desilylation of Silylamines by Singlet Oxygen

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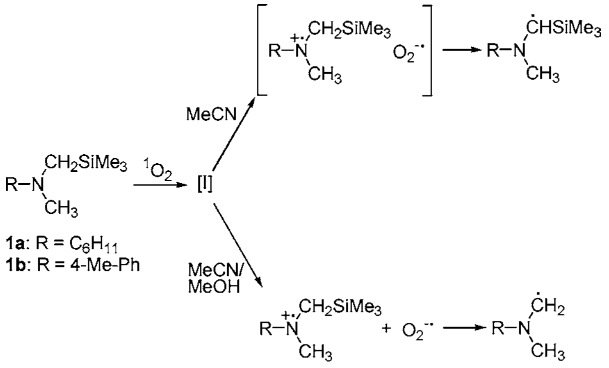
ABSTRACT

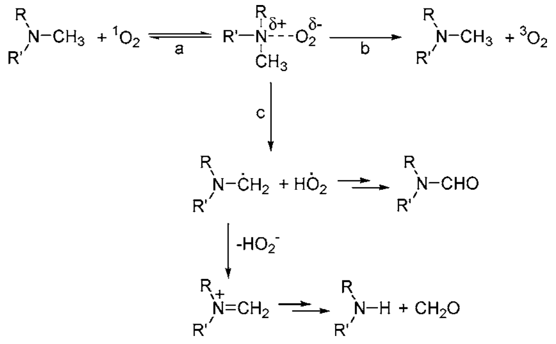


A kinetic and product study has been carried out for the reactions of silylamines 1a and 1b with $^1O_2$ in MeCN and (80:20) MeCN–MeOH. Indications suggesting an electron-transfer step following exciplex (I) formation have been obtained. However, the fate of the radical cation is solvent dependent. The radical cation undergoes desilylation in MeCN–MeOH and deprotonation in MeCN.

The capacity of tertiary amines to quench singlet oxygen, O_2 ($^1\Delta_g$), henceforth referred to as $^1O_2$, is well-known.[1] The reaction seems to involve the reversible formation of a charge-transfer complex which can proceed to the starting amine and the ground triplet state $O_2(^3\Sigma_g{}^-)$, henceforth indicated as O_2 (physical quenching), or to products (chemical quenching). Our recent work on the reaction of *N*,*N*-dimethylbenzylamine with $^1O_2$ has provided results that fit in with the picture reported in Scheme 1.[2]

The possibility of an electron-transfer step has also been considered,[3] but evidence in this respect has been presented only for the quenching in water by NADH[3a] and some aromatic amines of very low oxidation potential (less than 0.5 V vs SCE in water), based on the detection of the amine radical cation or $O_2{}^{\bullet-}$.[3b,c,e] However, no product study was

Scheme 1



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[1] (a) Gorman, A. A. *Adv. Photochem.* **1992**, *17*, 217. (b) Wilkinson, F.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1995**, *24*, 663. (c) Schweitzer, C.; Schmidt, R. *Chem. Rev.* **2003**, *103*, 1685 (d) Clennan, E. L.; Pace, A. *Tetrahedron* **2005**, *61*, 6665.

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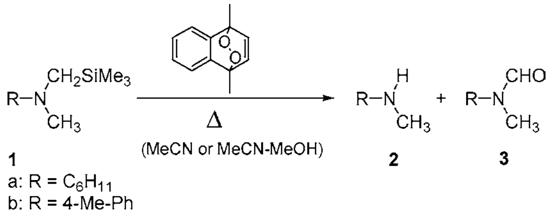
carried out in these cases and the extent of chemical quenching with respect to the overall (chemical + physical) quenching was very small. The solvent water appeared to play an essential role as no evidence for the electron-transfer mechanism was found in MeCN.

Also in view of the scarcity of detailed product studies for the reactions of amines with $^1O_2$,[1d] we have now extended our investigation to silylamines. These species have very low oxidation potentials (ca. 0.4 V lower than those of the corresponding amines. See Supporting Information) and easily form radical cations that undergo a very fast, nucleophilically assisted, cleavage of the C−Si bond.[4] Thus, we felt that these properties might significantly influence the extent of chemical quenching in the reaction with $^1O_2$ as well as the mechanism of product formation. On this basis, we have carried out a kinetic and products study of the quenching of $^1O_2$ in MeCN by *N*-methyl-*N*-(trimethylsilylmethyl)cyclohexylamine (**1a**) and *N*-methyl-*N*-(trimethylsilylmethyl)-*p*-toluidine (**1b**) (Scheme 2). In this paper, we wish to present the results of these investigations that suggest that these reactions involve an electron-transfer step.

Scheme 2



The reactions of **1a** and **1b** with $^1O_2$, thermally generated by 1,4-dimethylnaphthalene endoperoxide,[5] were carried out in dry MeCN[6] and in MeCN containing 20% (v/v) of methanol (henceforth referred to as MeCN−MeOH, for the sake of brevity). Using substrate 0.01 M and endoperoxide from 0.01 to 0.1 M (depending on the extent of chemical quenching),[7] significant product yields were observed (the conversion of starting amine ranging from 8.4 to 35%) indicating that, particularly with **1a**, chemical quenching of $^1O_2$ is an important fraction of the overall quenching. Products, yields (with respect to the amount of $^1O_2$ generated by the endoperoxide),[8] and fractions of chemical quenching (Q_c) are reported in Table 1 together with the rates of *total* quenching, k_Q (physical plus chemical), measured by time-resolved luminescence at 1270 nm. For comparison purposes, in Table 1 are displayed the data for the corresponding nonsilylated amines, *N*,*N*-dimethylcyclohexylamine (**4**) and *N*,*N*-dimethyl-*p*-toluidine (**5**).

Table 1. Oxygenation of Amines by $^1O_2$

			products[a] (yield, %)			
subst	solvent	k_Q (M^{-1} s^{-1})	**2**	**3**	CH_2O	Q_c[b] (%)
1a	MeCN[c]	1.5×10^8	19	2.1	*g*	21
	20% MeOH[c]	1.2×10^8	24	20	26	44
1b	MeCN[d]	9.4×10^8	1.2	*h*	*i*	1.2
	20% MeOH[e]	5.0×10^8	5.6	1.9	6	7.5
4	MeCN[e]	2.65×10^8	6.6	3.0	7	9.6
	20% MeOH[e]	1.5×10^8	11	*j*	12	11
5	MeCN[d]	1.0×10^{9}[f]	*h*	*h*		0
	20% MeOH[d]	6.2×10^8	*h*	*h*		0

[a] Referred to the amount of $^1O_2$ produced by the endoperoxide and determined by GC analysis (error ± 5%) except for CH_2O that was spectrophotometrically determined after treatment with the Nash reagent (error ± 5%). [b] Sum of the yields of **2** and **3** vs $^1O_2$. [c] Endoperoxide/amine = 1:1. [d] Endoperoxide/amine = 10:1. [e] Endoperoxide/amine = 2:1. [f] Reference 3e. [g] Product below the detection limit (3%). [h] Product below the detection limit (0.01%). [i] Product below the detection limit (0.3%). [j] Product below the detection limit (0.05%).

Considering first the kinetic results, it appears clear that in both MeCN and MeCN−MeOH the rate of quenching k_Q is very little affected by replacing H by the TMS group, which suggests that formation of the encounter complex, or exciplex, plays a kinetically important role with both amines and silylamines.[1a] Since the quenching rates of **4** and **5** are slightly higher than those of the corresponding silylamines, steric effect by TMS affecting the formation of the exciplex intermediate can be suggested.[9] Probably, the effect is larger than that inferred by the rate data in Table 1 since, as already said, the presence of the TMS group lowers the oxidation potential of the amine and this is expected to lead to an

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(5) (a) Turro, N. J.; Chow, M. F. *J. Am. Chem. Soc.* **1981**, *103*, 7218. (b) Adam, W.; Prein, M. *Acc. Chem. Res.* **1996**, *29*, 275. (c) Greer, A.; Vassilikogiannakis, G.; Lee, K.-C.; Koffas, T. S.; Nahm, K.; Foote, C. S. *J. Org. Chem.* **2000**, *65*, 6876. (d) Ben-Shabat, S.; Itagaki, Y.; Jockusch, S.; Sparrow, J. R.; Turro, N. J.; Nakanishi, K. *Angew. Chem., Int. Ed.* **2002**, *41*, 814. (e) Poon, T.; Turro, N. J.; Chapman, J.; Lakshminarasimhan, P.; Lei, X.; Jockusch, S.; Franz, R.; Washington, I.; Adam, W.; Bosio, S. G. *Org. Lett.* **2003**, *5*, 4951.

(6) Carefully dried by reflux on CaH_2.

(7) Under these conditions all the $^1O_2$ (k_d ca. 2×10^4 s^{-1} in MeCN)[1b] generated is quenched by the substrate (0.01 M, k_Q ca. 10^8 $M^{-1}s^{-1}$).

(8) (a) The yield of singlet oxygen generated from 1,4-dimethylnaphthalene endoperoxide in MeCN and in MeCN−MeOH at $T = 40$ °C was spectrophotometrically measured, according to a literature procedure,[3c,5a] using 1,3-diphenylisobenzofurane as singlet oxygen acceptor. It resulted to be 70% (in MeCN) and 80% (in MeCN−MeOH) vs the initial amount of endoperoxide, values very close to that previously observed in dioxane.[5a] These values are much larger than that (25%) reported by Günther et al.[8b] for the solvent MeCN at 20 °C, which was used in our previous work to calculate the chemical quenching of *N*,*N*-dimethylbenzylamine.[2] On the basis of the present value in MeCN, the actual chemical quenching of *N*,*N*-dimethylbenzylamine in MeCN is 3% and not 9% as reported. (b) Günther, G. S.; Lemp, E. M.; Zanocco, A. L. *J. Photochem. Photobiol. A* **2002**, *151*, 1.

(9) Monroe, B. M. *J. Phys. Chem.* **1977**, *81*, 1861.

increase in the quenching rate.[9,10] As expected,[11] a slight decrease in k_Q on passing from MeCN to protic MeCN−MeOH is observed.

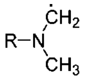
Whereas the kinetic effect is almost negligible, the data in Table 1 show that the TMS group has a very positive effect upon the extent of chemical quenching that significantly increases on passing from **4** to **1a** (from 9.6 to 21% in MeCN and from 11 to 44% in MeCN−MeOH) and from **5** to **1b** (from 0 to 1.2% in MeCN and from 0 to 7.5% in MeCN−MeOH). In the latter case, it has to be noted that *no* chemical quenching is observed with the nonsilylated amine in both solvents. Thus, the presence of the TMS group clearly favors more the path leading to products than that leading to physical quenching. Another observation is that the chemical quenching for the silylated amines is significantly higher in MeCN−MeOH than in MeCN, particularly with **1b**. With the non silylated amine **4**, very close values of Q_c are observed in the two solvent systems.

With respect to the products nature, the first observation is that complete desilylation is observed with both silylamines. In all cases but one (vide infra) the secondary amines **2a** and **2b** and the formamides **3a** and **3b** are formed from **1a** and **1b**, respectively. From **1a**, the main product in MeCN is **2a**, whereas **2a** and **3a** are formed in similar amounts in MeCN−MeOH. From **1b**, only **2b** is obtained in MeCN, but both **2b** and **3b** are obtained in MeCN−MeOH.

To have some information about the origin of the secondary amines we wanted to establish if CH_2O is also formed in the oxygenation reactions. The result of this search was most interesting as we found (data included in Table 1) that CH_2O is formed *only* in MeCN−MeOH, where it is obtained in amounts corresponding to those of the secondary amine (**2a** from **1a** and **2b** from **1b**). In MeCN only traces of CH_2O were observed.[12] With the nonsilylated amine 4, formaldehyde is formed in the expected amount (Scheme 1) both in MeCN and MeCN−MeOH.

This finding allows the important conclusion that whereas in MeCN-MeOH the precursors of **2a** and **2b** are certainly the α-amino carbon radicals **6a** and **6b**, respectively (that also produce the corresponding formamides, as shown in Scheme 1), the two secondary amines *must* be formed by a different pathway in MeCN.

This solvent-dependent mechanistic dichotomy can be reasonably interpreted into the framework of the mechanistic scheme proposed by Mariano et al. for the photoinduced electron-transfer reactions of silylamines.[4a,b] The key point in this scheme is that silylamine radical cations can undergo desilylation or deprotonation depending on whether they are formed as solvated ions or intimate ion pairs, respectively.

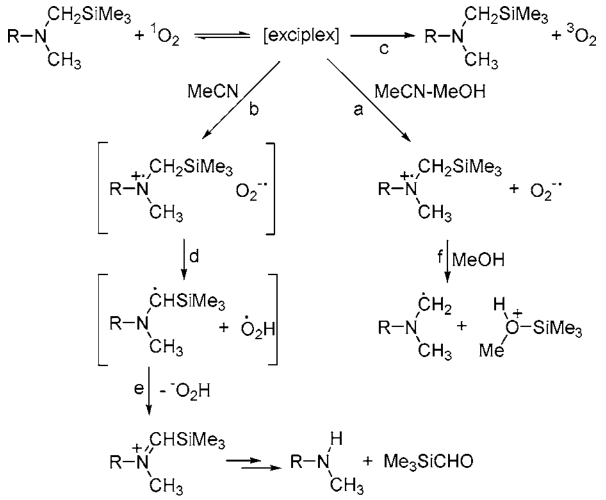


6a R = C_6H_{11}

6b R = 4-Me-Ph

On this basis, the clean desilylation reaction observed by us in MeCN−MeOH strongly suggests the operation of an electron transfer (ET) mechanism where the presence of the protic solvent favors the evolution of the exciplex to a pair of solvated ions. The formed free silylamine radical cation can undergo attack at silicon by MeOH, a strong silicophilic species. Desilylation occurs with formation of carbon radicals **6** (Scheme 3, path f). The latter may then form the secondary amine and the formamide, as described in Scheme 1 for the nonsilylated amine.[13,14]

Scheme 3



The above hypothesis is supported by the results of the photolysis of **1a** sensitized by 1,4-dicyanonaphthalene (DCN) in MeCN−MeOH, reported in in Table 2.[15] This process occurs by an electron transfer mechanism and moreover it ultimately leads to the formation of $O_2^{\bullet -}$ (Scheme 4), as in ET oxygenations by $^1O_2$. It can be immediately seen that the outcome is the same as that observed in the reactions

Table 2. Photooxidation of **1a** Sensitized by DCN in O_2 Saturated Solution[a]

solvent	yield[b] (%)		
	2a	**3a**	CH_2O
20% MeOH	25	20	27
MeCN	5	2	-[c]

[a] Irradiated at 365 nm for 10 min. Substrate/sensitizer 10:1. [b] Referred to the initial amount of substrate. [c] Cyclohexanone (30%) was the main product.

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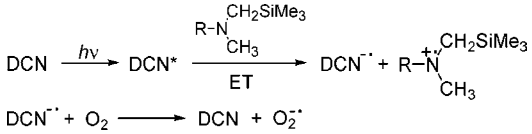
(10) (a) Furukawa, K.; Ogryzlo, E. A. *J. Photochem.* **1972**, *1*, 163. (b) Young, R. H.; Brewer, D.; Kayser, R.; Martin, R.; Feriozi, D.; Keller, R. A. *Can. J. Chem.* **1974**, *52*, 2889.

(11) Clennan, E. L.; Noe, L. J.; Wen, T.; Szneler, E. *J. Org. Chem.* **1989**, *54*, 3581.

(12) Experiments were also carried out at concentrations of MeOH lower than 20%, but it was noted that with less than 10% of MeOH the products mixture was complicated by the reaction of the *N*-methylamines **2** with CH_2O. Probably, at higher MeOH concentration, CH_2O is completely in the acetal form and the above reaction does not occur.

(13) $O_2^{\bullet -}$ can reasonably be protonated by $Me_3SiO(H)Me^+$ giving $HO_2^{\bullet}$ that, by reaction with the carbon radical **6**, forms **2** and **3** as described in Scheme 1.

Scheme 4



with $^1O_2$. Accordingly, the secondary amine and the formamide are formed, in a 25:20 ratio very close to that (24:20) found in the reaction with $^1O_2$ (Table 1).

In dry MeCN, instead, as also suggested by Mariano et al., the ET step leads to an intimate ion pair (Scheme 3, path b) which undergoes deprotonation involving the more acidic C−H bond, that is the one α to silicon (Scheme 3, path d). The α-trimethylsilyl substituted carbon radical may then be oxidized (presumably by $^{\bullet}O_2H$) to form the secondary methylamine (**2a** or **2b**) as the main reaction product (Scheme 3, path e). In this process, Me_3SiCHO, a very elusive species due to its high oxidizability, should be formed[16] and not CH_2O.[17]

We have also performed the DCN-sensitized photolysis of **1a** in MeCN. In this case, however, the results (Table 2) are significantly different with respect to those for the reaction with $^1O_2$, but it should be considered that a different ion pair ($DCN^{\bullet -}$ in the place of $O_2^{\bullet -}$) may be formed in the DCN-sensitized photolysis. Interestingly, the deprotonation by $DCN^{\bullet -}$ inside the ion pair appears to involve mainly the tertiary C−H of the cyclohexane ring, as clearly shown by the predominant formation of cyclohexanone. Anyway, this result confirms that **1a** radical cation undergoes desilylation in MeCN−MeOH and deprotonation in MeCN, as found in the reaction with $^1O_2$.

Finally, a further, even though indirect, support to the ET step in the reaction of silylamines with $^1O_2$ comes by looking at the data for the nonsilylated amines that should react by the hydrogen atom transfer (HAT) mechanism shown in Scheme 1. It can be noted that with both **4** and **5** there is no increment in the extent of chemical quenching on going from MeCN to MeCN−MeOH, which contrasts with the significant increase noted with **1a** and **1b**. Clearly, no important solvent effect can be predicted for a HAT mechanism, whereas significant effects are reasonably expected for an ET mechanism.[18]

In conclusion, evidence has been presented showing the operation of dual pathways for the reaction of $^1O_2$ with silylamines. An electron-transfer mechanism is suggested leading to a silylamine cation radical that undergoes a different fate (desilylation vs proton abstraction) depending on whether it is formed inside an intimate ion pair (dry MeCN) or as a solvated ion radical (MeOH−MeCN).

Acknowledgment. MIUR, University “La Sapienza” of Rome, and University of Perugia are thanked for the financial support.

Supporting Information Available: Experimental details, determination of amine oxidation potentials, and measurement of the quenching rate constant of $^1O_2$ by **1a**, **1b**, **4**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) (a) E_p values for **1a** and **1b** in MeCN are around 0.5 V vs SCE (see the Supporting Information); the reduction potential of $^1O_2$ in the same solvent is 0.11 V vs SCE[14b] but higher values are expected in MeCN−MeOH in view of the greater stability of $O_2^{\bullet -}$ in the protic mixture. (b) Fukuzumi S.; Fujita, S.; Suenobu, T.; Yamada, H.; Imahori, H.; Araki, Y.; Ito, O. *J. Phys. Chem. A* **2002**, *106*, 1241.

(15) **1b** underwent a light induced decomposition in the absence of the sensitizer.

(16) (a) Banik, G. M.; Silverman, R. B. *J. Am. Chem. Soc.* **1990**, *112*, 4499. (b) Silverman, R. B.; Lu, X.; Banik, G. M. *J. Org. Chem.* **1992**, *57*, 6617.

(17) (a) One might suggest that Me_3SiCHO is also formed in MeCN−MeOH where, however, it undergoes the Brook rearrangement to form CH_2O observed under those conditions.[17b] Since only traces of deuterium were incorporated in CH_2O formed when the oxygenation was carried out in MeCN−MeOD, this possibility represents a very minor pathway. (b) Brook, A. G. *Acc. Chem. Res.* **1974**, *7*, 77.

(18) Of course, it is also possible that the mechanism in MeCN is different from that in MeCN−MeOH, involving a HAT inside the exciplex itself (as in the case of nonsilylated amines) involving the α-TMS substituted C−H bond. At present, we cannot exclude this possibility even though, on the basis of the close parallelism between our results and those by Mariano, it is likely that the same mechanism (ET) is operating in the two solvent systems.